

# <sup>1</sup> HYDROTALCITE-LIKE COMPOUNDS, SOLID-BASE CATALYSTS FOR CYANOETHYLATION REACTION

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**abstract:** The layered double hydroxide (LDH) with chemical composition  $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$  was prepared via a wet chemical route of gel to crystallite conversion. This solid-base compound and the mixed oxides resulting by LDH calcination were characterised by XRD, FT-IR and porous structure and then tested in the cyanoethylation of ethanol with acrylonitrile reaction. The catalytic activity was compared with those obtained using catalyst samples  $\text{Li}/\text{Al}(\text{OH})_3$ ,  $\text{Li}/\text{Al}_2\text{O}_3$ ,  $\text{Na}/\text{Al}_2\text{O}_3$ ,  $\text{K}/\text{Al}_2\text{O}_3$  prepared by wet impregnation.

**keywords:** Li-Al hydrotalcite, mixed oxides  $\text{Me}^1/\text{Al}_2\text{O}_3$  ( $\text{Me}^1 = \text{Li}, \text{Na}, \text{K}$ ), cyanoethylation reaction

## Introduction

Much attention has been paid over a recent years to the establishments of ecologically acceptable processes in the chemical synthesis. Therefore, the use of basic solid catalysts as hydrotalcite-like compounds (HT) and admixture of oxides obtained by calcinations of hydrotalcite (CHT) is an area of growing interest due to the following advantages: easy separation of catalysts from the reaction mixture, reusable catalysts, easy modification of the basic strength sites and their pore structure [1, 2, 3, 4].

Hydrotalcites consist of brucite-like layers having positive charge with anionic species in the interlayer, forming neutral materials with the general formula:  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}] \cdot m\text{H}_2\text{O}$  where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are respectively divalent and trivalent metal like  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ,  $\text{A}^{n-}$  is an anion and  $x$  can have values between 0.2-0.33 [5].

The possibility of preparing hydrotalcites with nominal composition  $[\text{M}^{1+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{(2x-1)+}[\text{A}^{n-}_{2x-1/n}] \cdot m\text{H}_2\text{O}$  is limited only to  $\text{Li}^+$  which has an anionic radius comparable to that of  $\text{M}^{2+}$  even the HT structure presents important differences in comparison with Mg-Al hydrotalcites [2]. With other monovalent cations, the corresponding double hydroxycarbonates of aluminium are dawsonite-type compounds [6].

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In the conventional (HT) the  $M^{2+}$  and  $M^{3+}$  occupy the some set of octahedral sites and there is no evidence for ordering of the cations. In the Li-Al (HT), the structure is constituted by the layer containing the cations in which Al octahedral are arranged as in gibbsite and the octahedral vacancies are filled by lithium ions [7].

Mg-Al hydrotalcites [8] and modified Mg-Al HT with Y, Gd, Sm, Dy or La ions [9, 10] and the corresponding mixed oxides obtained by calcinations of HT precursors act as base solid catalysts for the cyanoethylation of ethanol with acrylonitrile under mild reaction conditions and there are reusable without an appreciable loss of activity and selectivity. This conjugated addition gives  $\beta$ -ethoxypropionitrile which can be converted to a carboxylic acid by hydrolysis and into corresponding amine by reduction, giving compounds of industrial interest for drug intermediates [9, 10].

Combination of different elements for HT synthesis, changing the element ratios in the brucite-like layer, selection of different anionic species and modified HT by addition of alkali cations, can tune up the basicity of HT, the interlayer distance and the catalytic properties.

Here we report the results of preparation of Li-Al HT and the corresponding mixed oxides obtained by calcinations of HT precursors and their structural properties in correlation of their activity and selectivity in the cyanoethylation of ethanol with acrylonitrile. The catalytic performances of the modified  $Al(OH)_3$  and  $Al_2O_3$  by addition of Li, Na, K ions (5% w/w) have been also studied in the cyanoethylation reaction.

## Experimental

### Catalysts preparation.

A layered double hydroxide with chemical composition  $LiAl_2(OH)_7 \cdot 2H_2O$  was prepared by a wet chemical route of gel to crystallite conversion at 80°C involving the reaction of hydrated alumina gel  $Al_2O_3 \cdot yH_2O$  ( $80 < y < 120$ ) with LiOH ( $Li_2O/Al_2O_3 > 0.5$ ) in presence of hydrophilic solvents such as ethanol under refluxing conditions.

The hydrated alumina gel were obtained by addition of concentrated ammonia solution (25% w/w) to an aqueous solution of  $Al(NO_3)_3 \cdot 9H_2O$  till the pH was 8.0. The  $Al(OH)_3$  gel was filtered, washed free of anion using hot and demineralized water, then was dried at 90°C for 12 hours.

To obtain Li-Al HT the  $Al(OH)_3$  gel was suspended in a conical flask containing an ethanolic solution of lithium hydroxide (four-fold excess of Li over the aluminum content  $Li/Al=4$  in 50 ethanol and 50 % water). The reaction vessel was fitted with a water-cooled condenser an alkali guard tube to prevent the contamination of  $CO_2$  and refluxed for 8 hours under continuously magnetic stirring. The solid product obtained was washed free of unreacted LiOH (pH $\approx$ 8-8.5) then filtered and dried at 90°C for 24 hours. The mixed oxides were obtained by calcinations the dried hydrotalcite Li-Al at 460°C for 18 hours under nitrogen flow. In order to check whether the catalysts  $Li/Al_2O_3$  obtaining by wet impregnation present different activity and selectivity in the cyanoethylation of ethanol with acrylonitrile by comparison of dried and calcinated Li-Al HT were prepared samples

containing 5% Li (w/w) by wet impregnation of  $\text{Al}(\text{OH})_3$  and respectively  $\gamma\text{-Al}_2\text{O}_3$  with aqueous solution of  $\text{Li}(\text{OH})$ . Also samples with 5% Na and respectively K on alumina. After impregnation the samples were dried at  $70^\circ\text{C}$  for 12 hours and then calcined at  $460^\circ\text{C}$ , 3 hours in air flow.

### **Catalysts characterization**

The X-ray diffractions (XRD) patterns were recorded on a computer controlled DRON-3 X-ray diffractometer equipped with a graphite monochromator using the  $\text{CuK}_\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) in a  $2\theta$  range of  $7\text{-}90^\circ$ , a step width of  $0.05^\circ$  and an acquisition time of 2s on each step.

Surface area were determined from  $\text{N}_2$  adsorption-desorption isotherms, using BET equation.

FT-IR spectra was recorded by spectrometer BioRad FTS 135 using KBr pellet techniq. The specter was recorded between  $400 - 4000 \text{ cm}^{-1}$ .

### **Catalytic measurements**

A typical procedure for the cyanoethylation of ethanol with acrylonitrile: into a reaction vessel equipped with a reflux condenser were successively placed the catalyst (0.0711g) ethanol (0.03 mmol; 1.7 ml) and acrylonitrile (0.01 mmol; 0.65 ml). The resulting mixture was stirred and heated on a silicon oil bath and refluxed for 5 hours. The conversion and selectivity of acrylonitrile into  $\beta$ -ethoxypropionitrile were determined by GC analysis using a Thermoquest equipment with a FID detector and a capillary column (30 m length; i.d. 0.324 mm) with DB-5 stationary phase.

## **Results and discussion**

The porous structure of catalysts containing lithium are reported in Table 1.

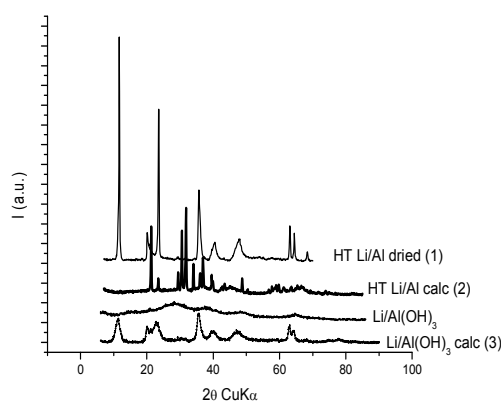
**Table 1. Porous structure of calcinated catalysts containing lithium**

Sample	$\text{Li}_2\text{O}\cdot 2\text{Al}_2\text{O}_3$	$\text{Al}(\text{OH})_3+\text{LiOH}$	$\text{Al}_2\text{O}_3+\text{LiOH}$
Surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )	163	196	178
Pore volume ( $\text{m}^3\cdot\text{g}^{-1}$ )	0.1587	0.2487	0.2336
Mean pore size ( $\text{\AA}$ )	22	36	27

Figure 1 presents the XRD patterns of the Li based catalysts samples prepared as below along with their corresponding calcinated samples. The XRD patterns shows:

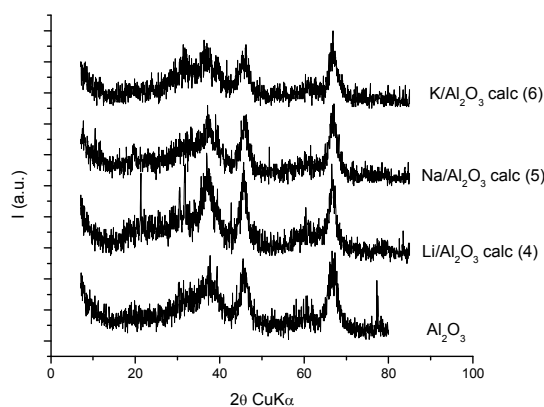
- The Li based catalyst has the structure of a layered double hydroxide of  $\text{LiAl}_2(\text{OH})_7\cdot 2\text{H}_2\text{O}$  type ( JCPDS 40-0710). ( denoted HT Li/Al dried (1))
- Its calcinated form (HT Li/Al calc. (2)) presents a mixture of very fine particles of a poor crystallized  $\gamma\text{-Al}_2\text{O}_3$  phase and large crystallites of a  $\text{Li}_2\text{CO}_3$ -zabeyelite phase (JCPDS 22-1141).
- The Li based catalyst prepared by impregnation on a boehmite type  $\text{AlO}(\text{OH})$  presents the structure of this boehmite phase with very broad peaks ( $\text{Li}/\text{Al}(\text{OH})_3$ ).

- Its calcinated form ( $\text{Li/Al(OH)}_3$  (3)) shows the formation of the structure of a layered double hydroxide of  $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ . The LDH phase is poor crystallized and presents broader peaks characteristic of a material with very small crystallites. An amorphous mixed oxides phase is to be presume as the background is very high and the peak intensities of the  $\text{Li/Al-LDH}$  phase are lower.



**Fig. 1.** The XRD patterns of the Li based catalysts samples along with their corresponding calcinated samples.

The XRD patterns of the Li, Na and K supported on  $\gamma\text{-Al}_2\text{O}_3$  ( $\text{Li,Na,K/Al}_2\text{O}_3$  (4,5,6)) are shown in figure 2. The patterns shows the preservation of the a  $\gamma\text{-Al}_2\text{O}_3$  phase with no by-products originated from deposited phase, except for Li case. For Li on a  $\gamma\text{-Al}_2\text{O}_3$  very fine particle of  $\text{Li}_2\text{CO}_3$ -zabeyelite phase (JCPDS 22-1141) are detected. The results account for the a highly dispersion of the active phase on the  $\gamma\text{-Al}_2\text{O}_3$  support, probably due to the mesoporous properties of the  $\gamma\text{-Al}_2\text{O}_3$  selected.



**Fig. 2.** The XRD patterns of the Li, Na and K supported on  $\gamma\text{-Al}_2\text{O}_3$

The FT-IR spectra of  $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$  HT is shows in figure. 3.

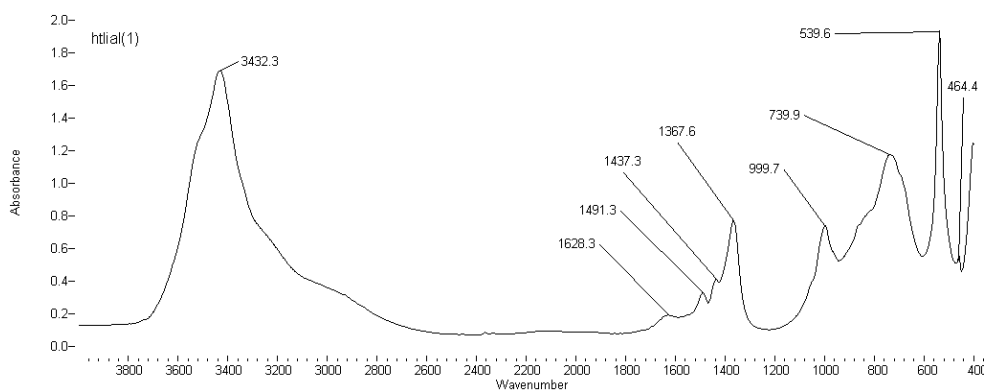


Fig. 3. The FT-IR spectra of  $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$  HT

The IR absorption spectra for the sample heated to  $100^\circ\text{C}$  shows a broad absorption band centered at  $3432\text{ cm}^{-1}$  owing to the O-H stretching frequencies from hydrogen bonded as well bridged hydroxy groups. Sharp peaks at  $1000$ ,  $740$  and  $539\text{ cm}^{-1}$  are characteristics of  $\text{AlO}_6$  octahedra.

For the sample heated to  $250^\circ\text{C}$  the band at  $3432\text{ cm}^{-1}$  is reduced in intensity because the hydroxy groups are removed.

The peak at  $1367\text{ cm}^{-1}$  vanishes, a doublet appears at  $1550\text{ cm}^{-1}$  and a new peak was observed at  $1200\text{ cm}^{-1}$ . Also the number of peaks between  $1000$  and  $500\text{ cm}^{-1}$  reduced to one centered around  $550\text{ cm}^{-1}$ .

The results of the thermal analyses are giving in figure 4.

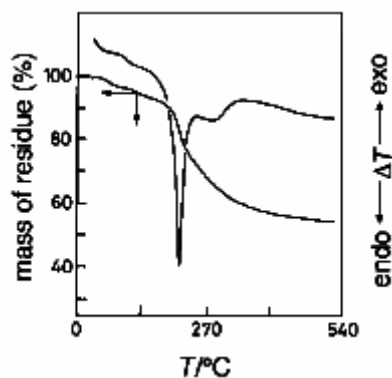


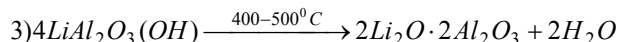
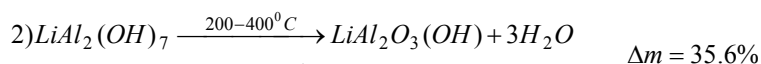
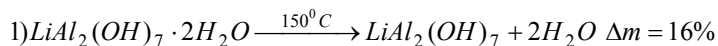
Fig. 4. DTA traces of  $\text{LiAl}_2(\text{OH})_7$

It has shown that for the dried Li-Al HT a total mass loss of ca. 51-54% up to  $540^\circ\text{C}$  is in a good agreement with data previously reported [11, 12].

The mass loss (5-8%) below  $100^\circ\text{C}$  is due to the loss of physically adsorbed water.

Between  $100$  and  $200^\circ\text{C}$  a 16% mass loss accompanied by a very strong endothermic peak in the DTA is due to the removal of the structural water.

Between 200 and 500°C the mass loss (ca. 30%) is for the dehydroxylation of surface; DTA shows a broad and shallow endothermic effect centered around 270°C. Probable the following reaction occurs:



The Li content, determined by wet chemical analysis using atomic absorption spectroscopy (AAS) for the dried and respectively calcinated sample were 3.84% and respectively 5.62% (w/w), in good agreement with these thermal transformations.

Figure 5 shows the catalytic activity of these solid-base catalysts represented as the acrylonitrile conversion.

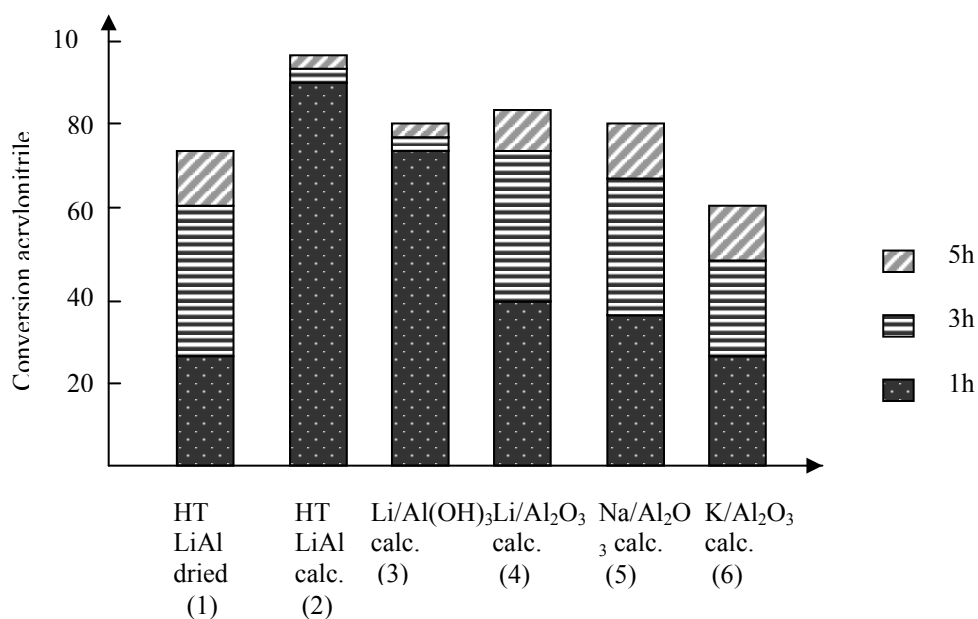


Fig. 5. The variation of acrylonitrile conversion against the reaction time

Although there are no significant difference of porous structure between the catalysts containing lithium a very important parameter of catalytic activity appeared to be the nature of precursors. The dried  $\text{LiAl}_2(\text{OH})_7$  sample shows a low activity even after five hours reaction time. High activity is characteristic of the calcined Li-Al LHD ( $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3$ ) which provides 97% acrylonitrile conversion and 93% after one hour reaction time.

A similar behavior is shown for the sample obtained by impregnation of  $\text{Al}(\text{OH})_3$  with  $\text{LiOH}$  solution even the total conversion after five hours did not exceed 79%.

Low reaction rate is proper for the catalyst obtained by impregnation of  $\text{Al}_2\text{O}_3$  with LiOH solution even the final conversion after five hours rises up to 84%. A similar behavior was shown for the catalysts Na- $\text{Al}_2\text{O}_3$  and K- $\text{Al}_2\text{O}_3$ . The activity of the catalysts which decreased with increasing the strength basicity of alkaline oxides suggested that the cyanoethylation reaction is catalyzed by the weak and medium basic sites.

For all catalysts the selectivity of  $\beta$ -ethoxypropionitrile was 100%.

Because the preparation of precursors  $\text{LiAl}_2(\text{OH})_7$  and  $\text{LiOH}/\text{Al}(\text{OH})_3$  for catalysts (2) respectively (3) used  $\text{Al}(\text{OH})_3$  and aqueous LiOH solution and quite similar conditions of preparation justify the high initial rate of reaction is due to some amount of  $\text{LiAl}_2(\text{OH})_7$  in the catalyst (2) composition (as is attested by the XRD measurements). The high activity of catalyst (2) obtained by calcinations of  $\text{LiAl}_2(\text{OH})_7$  precursor is probably a result from a highly disordered structure, small size crystals, accessibility of the active basic sites and the defect sites induced by lithium insertion in  $\text{Al}_2\text{O}_3$  structure. All these elements could lead to synergistic effects.

## Conclusions

Li-Al LDH is an effective precursor for the manufacturing of mixed oxides catalysts in the reaction of cyanoethylation of ethanol with acrylonitrile.

These results show that the main parameter of catalytic activity is the nature of precursors. The high activity of calcined catalyst is a result from a highly disordered structure, small size crystals, defect sites and a weak and medium basicity of solid.

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