



# Quaternary ammonium salts for hydrotalcite-type catalysts synthesis

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## Introduction

➤ There is a growing interest focused on the synthesis and properties of layered double hydroxides (LDH) as part of the anionic clays materials.

➤ The main method of preparation of LDH is still the co-precipitation by contacting an aqueous solution of the salts containing the target cations with an inorganic alkaline solution.

➤ However, it involves some disadvantages: multiple synthesis steps, high energy consumption, use of specific vessels in each stage of the process, etc.

➤ The mechano-chemical method is as an alternative to co-precipitation involving only one step mixing in a mortar/mill of all the reactants followed by washing and drying.

➤ The aim of this study was to perform a comparative analysis of the physico-chemical properties and catalytic activity of hydrotalcites prepared by co-precipitation and mechano-chemical methods in presence of organic alkalis. These catalysts were investigated in cyanoethylation reaction of ethanol with acrylonitrile toward 3-ethoxypropionitrile.

## Experimental

➤ The hydrotalcites  $Mg_{0.75}Al_{0.25}$  were obtained at pH 10 by co-precipitation of magnesium and aluminium nitrates and base solution (Tetra Methyl Ammonium Hydroxide and Tetra *n*-Butyl Ammonium Hydroxides) under low supersaturation (HT-MgAl-TMAH-CP; HT-MgAl-TBAH-CP).

➤ In the mechanochemical method, all precursors were mechanically mixed in a Mortar Grinder RM 200 (HT-MgAl-TMAH-MC; HT-MgAl-TBAH-MC).

➤ All dried samples were calcined in air atmosphere at 460°C (cHT-MgAl-TMAH-CP; cHT-MgAl-TMAH-MC; cHT-MgAl-TBAH-CP; cHT-MgAl-TBAH-MC).

➤ The resulted mixed oxides were then rehydrated in order to reconstruct the layered structure (hyHT-MgAl-TMAH-CP; hyHT-MgAl-TMAH-MC; hyHT-MgAl-TBAH-CP; hyHT-MgAl-TBAH-MC).

➤ The characterisation of samples has been carried out by XRD, DRIFT, BET, DTA-TG, irreversible adsorption of organic acids of different  $pK_a$  values.

➤ The cyanoethylation reaction were carried out 5h, reflux, ethanol/acrylonitrile = 3/1.

## Results

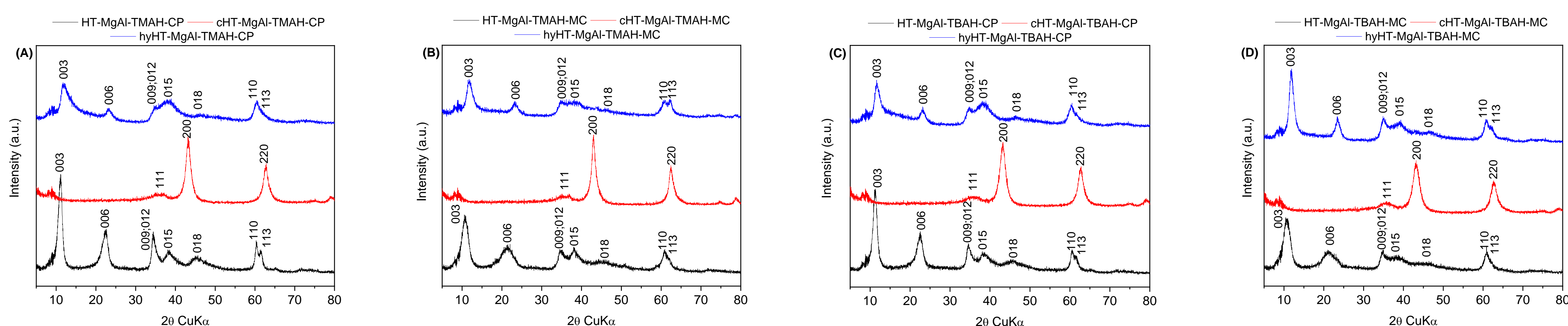
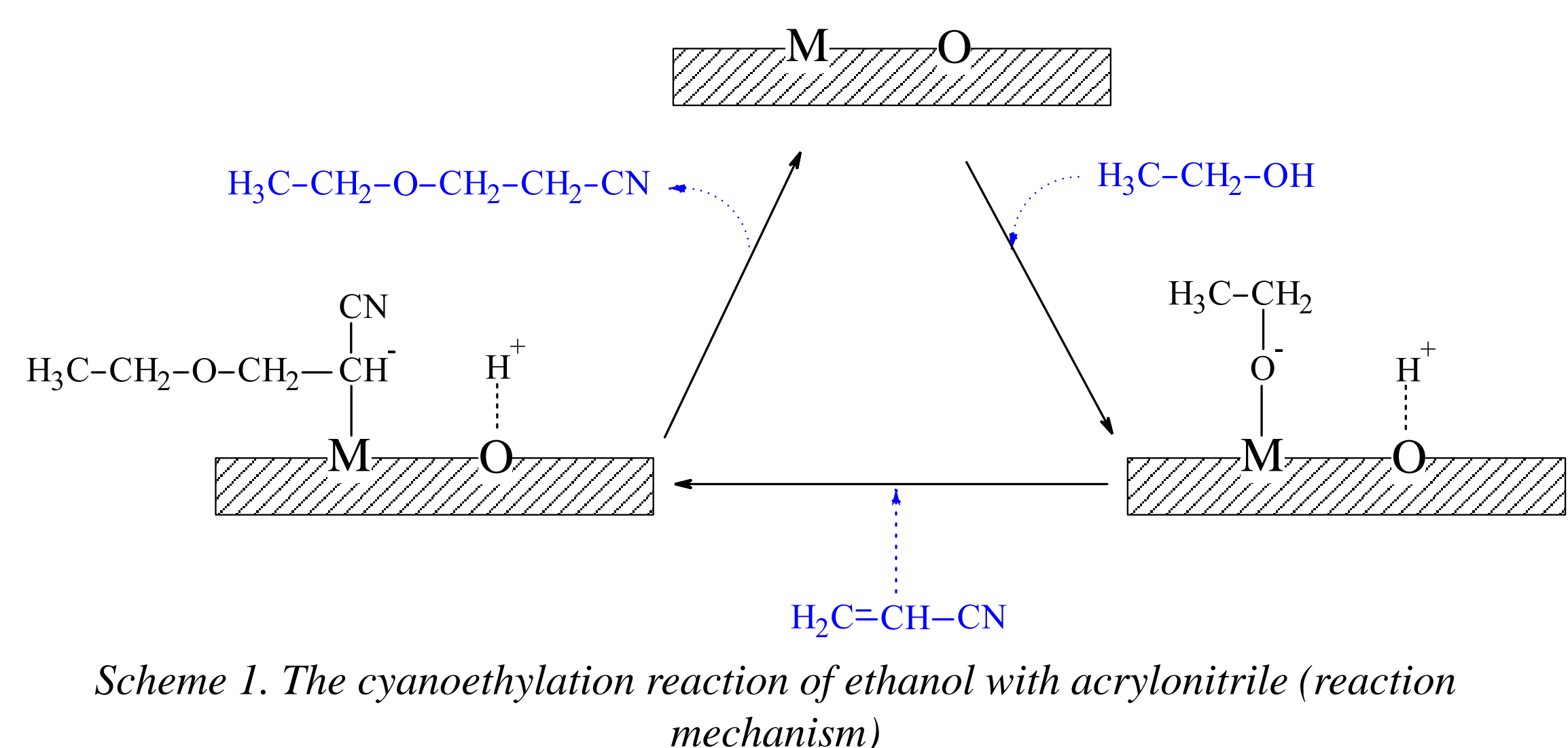


Figure 1. The XRD patterns of hydrotalcite, mixed oxides and reconstructed samples for: (A) TMAH as hydrolysis agent and co-precipitation method; (B) TMAH as hydrolysis agent and mechano-chemical method; (C) TBAH as hydrolysis agent and co-precipitation method; (D) TBAH as hydrolysis agent and mechano-chemical method

Samples	Surface area (m <sup>2</sup> ·g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )	Average pore width (Å)	Total number of base sites (mmol·g <sup>-1</sup> )*	Distribution of base sites	
					Strong base sites (mmol·g <sup>-1</sup> **)	Weak and medium base sites (mmol·g <sup>-1</sup> ***)
HT-MgAl-TMAH-CP	1.7	0.0054	126.65	6.83	0.30	6.53
cHT-MgAl-TMAH-CP	189.1	0.3585	75.84	8.39	0.39	8.00
hyHT-MgAl-TMAH-CP	0.5	0.0039	324.28	7.23	0.35	6.88
HT-MgAl-TMAH-MC	4.8	0.0118	99.04	6.68	0.25	6.43
cHT-MgAl-TMAH-MC	197.8	0.3185	64.41	8.20	0.35	7.85
hyHT-MgAl-TMAH-MC	1.1	0.0038	142.77	7.05	0.28	6.77
HT-MgAl-TBAH-CP	3.2	0.0077	97.89	7.03	0.32	6.71
cHT-MgAl-TBAH-CP	191.2	0.3466	74.33	8.40	0.39	8.01
hyHT-MgAl-TBAH-CP	1.4	0.0040	163.54	7.26	0.37	6.89
HT-MgAl-TBAH-MC	9.9	0.0189	76.09	6.70	0.27	6.43
cHT-MgAl-TBAH-MC	199.5	0.3022	63.87	8.30	0.37	7.93
hyHT-MgAl-TBAH-MC	0.8	0.0014	93.89	7.19	0.37	6.82

\*AA = acrylonitrile, TMAH = phenol, TBAH = phenol  
\*\* equal to the difference: Total number of base sites - Strong base sites  
\*\*\* equal to the difference: Total number of base sites - Strong base sites

Table 1. The surface area and basicity of materials



Scheme 1. The cyanoethylation reaction of ethanol with acrylonitrile (reaction mechanism)

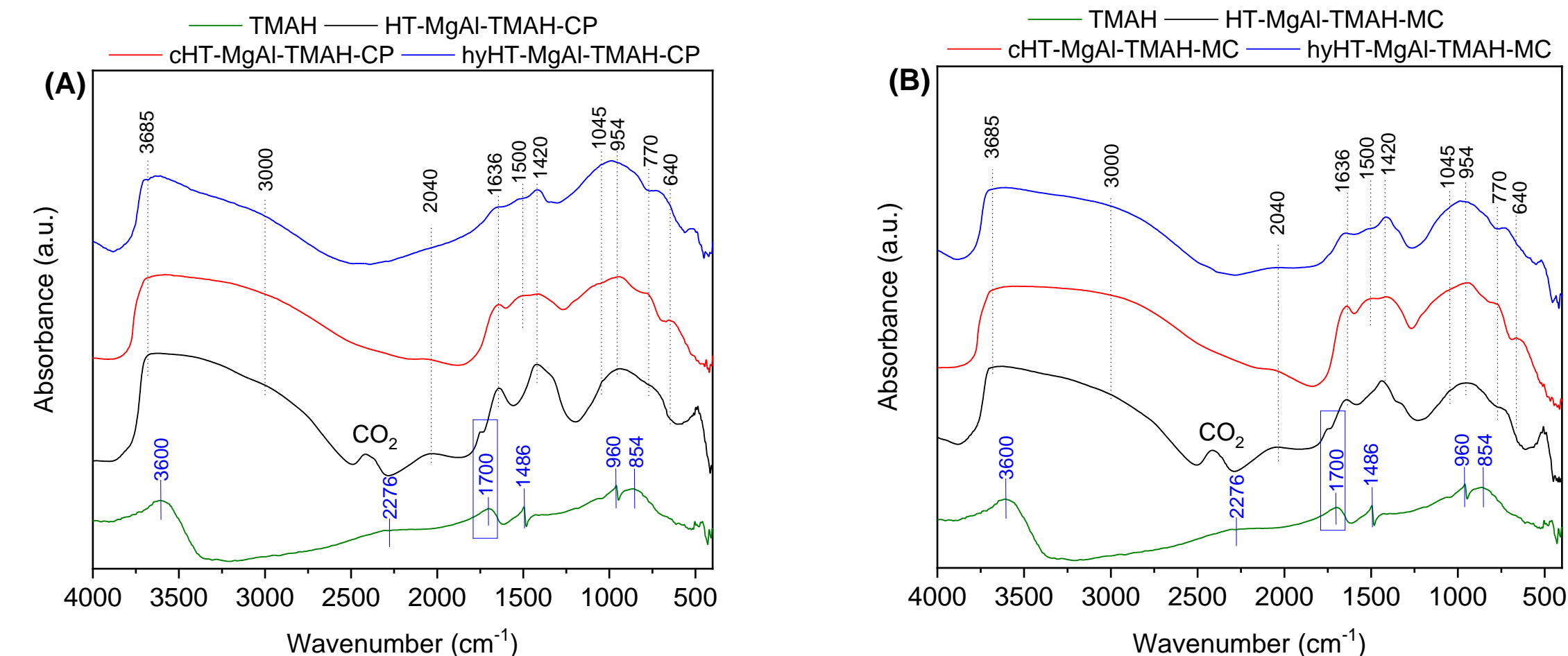


Figure 2. The DRIFT spectra of hydrotalcite, mixed oxides and reconstructed sample for: (A) TMAH as hydrolysis agent and co-precipitation method; (B) TMAH as hydrolysis agent and mechano-chemical method

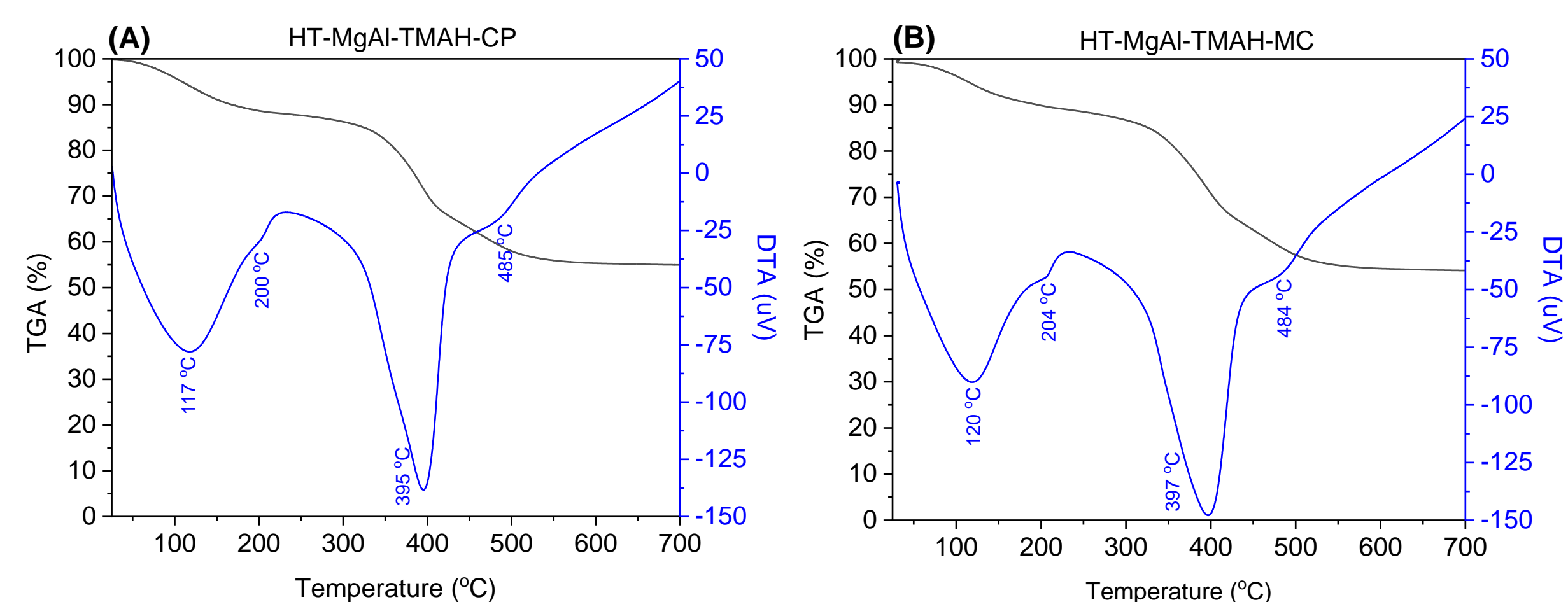


Figure 3. The TGA-DTA profiles of hydrotalcite, mixed oxides and reconstructed sample for: (A) TMAH as hydrolysis agent and co-precipitation method; (B) TMAH as hydrolysis agent and mechano-chemical method

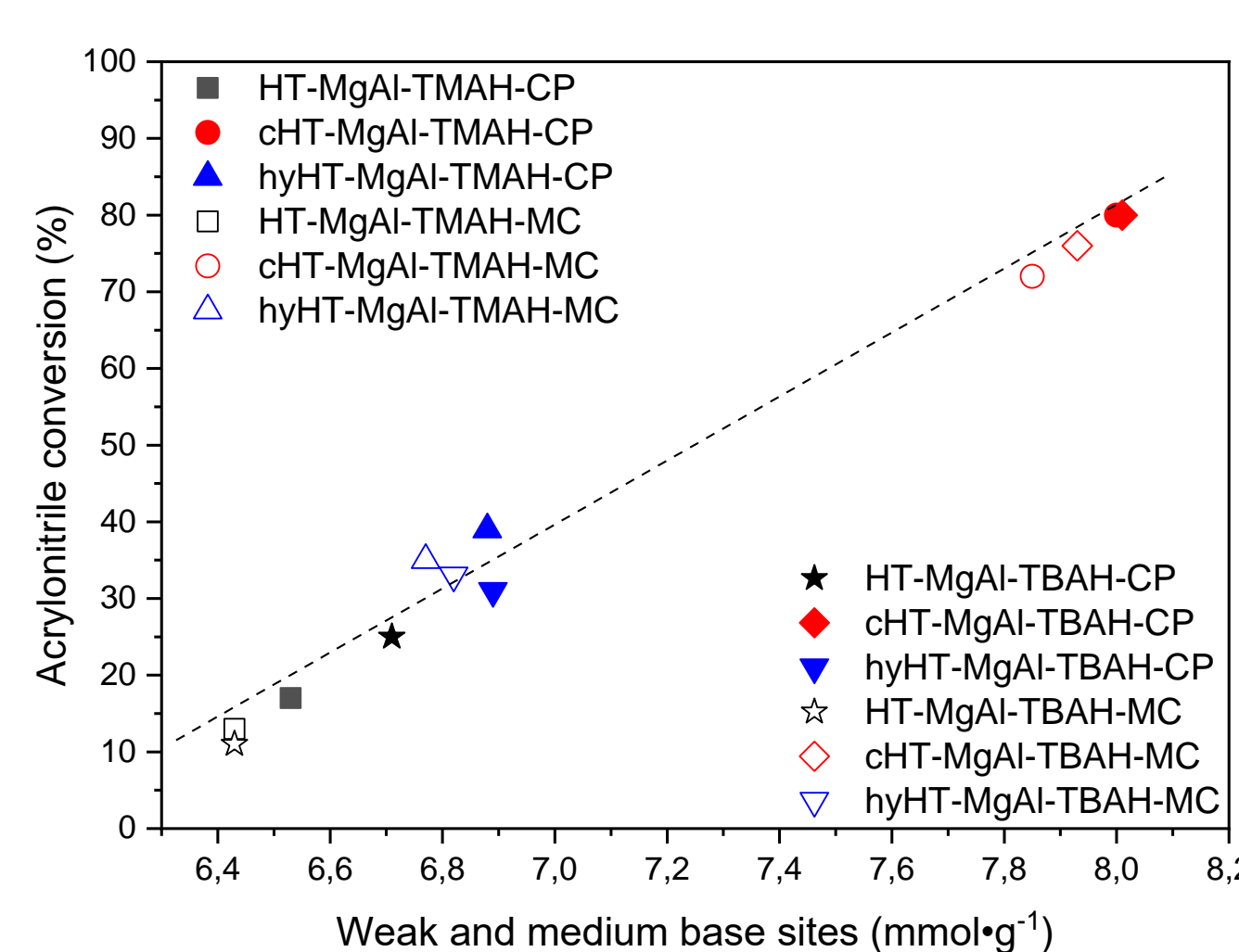


Figure 4. The variation of the acrylonitrile conversion after 5h reaction time vs. weak and medium basicity of the investigated catalysts

100% selectivity  
3-ethoxypropionitrile

## Conclusion

➤ TMAH and TBAH represent a viable alternative to traditional inorganic alkalis for hydrotalcite Mg/Al synthesis.

➤ The economy of distilled water used to wash the gel obtained as well as the total absence of alkaline cations.

➤ The catalytic activity followed the trend: mixed oxides > reconstructed samples > dried samples depending on the variation of weak and medium base sites.

➤ The selectivity towards 3-ethoxypropionitrile is 100%.

## Acknowledgements

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI – UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0387/ 80PCCDI, within PNCDI III.