

Hydrotalcite-like compounds as catalysts in liquid phase organic synthesis

I. Knoevenagel condensation promoted by



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Abstract

Ni–Al hydrotalcite-like compounds, obtained by precipitation from homogeneous solution accomplished by urea hydrolysis, have been characterised for chemical composition, BET specific surface area, X-ray diffraction and thermogravimetry. The base strength of surface sites was estimated with the method of adsorbed acid–base indicators. A sample of formula $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135}$, previously dried at 150 °C, has been used as base catalyst at 60 °C in absence of solvents in the Knoevenagel condensation of different aldehydes with malononitrile and ethylcyanoacetate. Aliphatic and aromatic aldehydes easily react in these reaction conditions and the Knoevenagel adducts were obtained in excellent yield, in short time. Dimethylmalonate, having methylene groups of very low acid strength ($\text{p}K_{\text{a}} > 13$) did not give the adduct with benzaldehyde because of not sufficiently high base strength of the hydrotalcite-like compound. The catalyst can be recycled several times, without loss of catalytic efficiency, and its performance has been compared with that of other heterogeneous base catalysts such as zeolite A, potassium exchanged zirconium phosphate, amberlist, modified hydrotalcites.

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1. Introduction

Recently, there has been an increasing interest on acid–base heterogeneous catalysts that can substitute liquid catalysts constituted by corrosive acids and bases in many chemical processes. The number of heterogeneous acid catalysts is very large and in-

cludes clays and modified clays [1] zeolites, acid oxides, heteropolyacids [2], organic polymers such as functionalized styrene–divinylbenzene resins [3]. In comparison, heterogeneous base catalysts are much less numerous, even if they are involved in many synthetic procedures. According to recent reviews [4,5], the common base catalysts are constituted by alkaline metal exchanged zeolites, alkaline earth metal oxides, KNH_2 or KF supported on alumina, supported alkali metals and mixtures of basic oxides obtained by calcination of hydrotalcite-like compounds. The catalytic

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efficiency of the above mentioned catalysts in various classes of reactions such as isomerizations, additions, alkylations is good. However, most of them suffers for air contamination since easily react with or adsorb water, carbon dioxide or other acidic gasses and vapours. In many instances it would be useful to have at disposal base catalysts that can be easily handled and do not require long procedures to be reactivated. In this context hydrotalcite-like compounds (HTlc) are of notable interest. HTlc are layered materials with general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}^{n-}]^{x-}\cdot mH_2O$, where M(II) may be Mg, Zn, Co, Cu, Fe, Ni, Mn; M(III) may be Al, Cr, Fe, V, Co. The layer structure arises from the concatenation of $M(OH)_6$ edge sharing octahedra. The isomorphous substitution of some divalent with trivalent cations generates positive charges balanced by A^{n-} anions (CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , organic anions) accommodated in the interlayer region, where co-intercalated water molecules are also located. The molar fraction $M(III)/M(III) + M(II)$ generally ranges between 0.2 and 0.33, and its value determines the charge density of the layer [6,7]. HTlc exhibit basic strength, sensibly lower than that of the mixed oxides obtained by thermal decomposition [8] but their handiness, stability and low activity allows a better control of the catalysed reactions. In addition, the basic properties of the HTlc may be modulated by replacing the carbonate anions with other counter-anions by simple ion exchange procedures. A research program has been undertaken to exploit the catalytic efficiency in liquid phase organic synthesis of HTlc converted in various salt forms. This paper reports the results obtained by using NiAl HTlc in carbonate form, that does not suffer from air contamination, as catalyst of the Knoevenagel condensation of aldehydes with active methylene compounds, such as malononitrile and ethylcyanoacetate. The Knoevenagel condensation has wide application in the synthesis of fine chemicals [9,10] and it is usually catalysed by bases [11,12] or acids [13,14] in homogeneous liquid phase systems. However, the use of heterogeneous catalysts (i.e. alumina [15], cadmium iodide [16], sepiolite [17], zeolites [18,19] clays [20], K^+ exchanged layered zirconium phosphate [21], anionic resin [22], N-bonded enolatorhenium(I) complex [23]) has been reported. Calcined MgAl HTlc has been used as catalyst of the ethyl acetoacetate–benzaldehyde condensation [24].

However, beside the Knoevenagel condensation, other reactions such as Michael addition, Claisen condensation, aldolic condensation also took place, probably because of the presence in the mixed oxides of sites with high basic strength [24]. Recently, other authors have used not thermal activated HTlc to carry out organic reactions in liquid phase [25,26].

2. Experimental

2.1. Synthesis of NiAl HTlc

Aqueous solutions, obtained by mixing 0.5 M $AlCl_3$ and 0.5 M $NiCl_2$ solutions in the proper amount to reach the chosen $Al(III)/Al(III) + Ni(II)$ molar ratio, were added of solid urea until the molar ratio urea/ $Al(III) + Ni(II)$ was 3.3. The solutions were kept at 100 °C under stirring for 3–6 days. The precipitation of NiAl hydrotalcite-like compounds was achieved by thermal hydrolysis of urea with formation of ammonium carbonate [27]. The precipitates obtained were separated from the mother solutions, washed with de-ionised water and with small volumes of 0.1 M sodium carbonate in order to exchange residue chloride ions, sometimes incorporated during the synthetic procedure, with carbonate anions. After the washings with Na_2CO_3 solutions the solids were recovered, washed with de-ionised water and finally dried at room temperature over P_4O_{10} .

2.2. Knoevenagel condensation

A mixture of active methylene derivatives (1 mmol) and catalyst NiAl HTlc (50 mg), previously dried in oven at 150 °C, was stirred at 60 °C under nitrogen. After 15 min, aldehyde (1 mmol) was added and the reaction mixture stirred for appropriate time. The mixture was then treated with dichloromethane (5 ml) and filtered. After evaporation of solvent, the Knoevenagel adduct was purified by chromatography.

2.3. Characterisation

The nickel and aluminium content of the HTlc was determined by standard EDTA titrations after having dissolved a weighed amount (about 100 mg) of the

sample in a few drops of concentrated HCl and having diluted with water to 50 ml.

The water content was obtained by thermogravimetric analysis performed with a Stanton-Redcroft STA 780 Analyzer at a heating rate of 2°/min under an air-flow. The differential scanning calorimetry curve, from room temperature up to 500 °C, was obtained with a Mettler-Toledo DSC 821 apparatus at the same heating rate.

The X-ray powder diffraction (XRPD) patterns of wet and dried samples were taken with a computer controlled Philips PW 1710 diffractometer, using the Ni-filtered Cu K α radiation and operating at 40 kV and 30 mA, step scan 0.03° 2 θ and 1 s counting time.

BET specific surface area was obtained by N₂ adsorption isotherms taken at 77 K with a Micromeritics ASAP 2010 instrument, after having degassed the sample for 1 day at 393 K. Particle-size distribution and scanning electron micrographs of the micro-crystals were taken with an AccuSizer TM 770 Optical Particle Sizer and a Philips XL30 microscope, respectively.

The evaluation of the surface basic strength of the HTlc has been obtained according to the Benesi method [28]. About 50 mg of the NiAl HTlc, previously heated at 150 °C, were dispersed in 10 ml of diethylether, under nitrogen. Few mg of indicator, with a chosen pK_a value, were then added to the dispersion and the colour change of the adsorbed indicator observed after 30 min.

¹H NMR spectra of CDCl₃ solutions of all organic compounds were recorded on a Bruker DPX spectrometer operating at 200.1 MHz in the Fourier transform mode. GC analyses and MS spectra were carried out with an HP 5890 gas chromatographer (dimethyl silicone column 12.5 m) equipped with an HP 5971 Mass Selective Detector. Flash column chromatography was performed on 0.040–0.063 mm (230–400 mesh ASTM) Merck silica gel.

3. Results and discussion

3.1. Preparation and characterisation of the catalyst

Several samples of NiAl HTlc have been prepared with the method of urea hydrolysis in aqueous solutions containing nickel and aluminium chlorides in the proper molar ratio. Table 1 reports the preparative conditions and the Al(Al + Ni) molar ratio in the obtained solids. Note that the molar ratio in the solid is always lower than that in the mother solution, approaching values near 0.25, that is one aluminium every three nickel ions in the brucite sheet. This arrangement seems to be the most stable and corresponds to that found in the mineral Takovite. All the samples have been equilibrated with a 0.1 M Na₂CO₃ solution to exchange residual chloride ions up-taken during the synthetic procedure. The specific surface area of the samples, previously degassed at 120 °C are reported in Table 1. It may be seen that the specific surface area decreases with increasing refluxing times and reach a maximum value for the sample with $x = 0.27$. It was thus decided to use this material as catalyst and to perform on it further characterisations.

The XRPD diffraction patterns of solid NiAl HTlc, shown in Fig. 1, revealed a high crystallinity and an interlayer distance of 7.94 Å. Fig. 2 shows the cumulative particle size distribution of the microcrystals. It may be seen that more than 85% of the particles have a diameter between 10 and 0.5 μ m. Observations at the scanning electron microscope showed that the particles are formed by almost spherical aggregates of hexagonal platelets (see Fig. 3a and b). Fig. 4 reports the weight loss curve as a function of temperature and the corresponding DSC curve. It may be seen that between 60 and 180 °C there is a broad endothermic peak related to loss of adsorbed and co-intercalated water. At temperatures higher than 300 °C both dehydroxylation and decarbonation reactions occur with a

Table 1

Effect of the metal ion molar fraction in solution and of reaction time on the composition and BET specific surface area of NiAl HTlc

Molar fraction in the solution Al(III)/Al(III) + Ni(II)	Molar fraction in the solid Al(III)/Al(III) + Ni(II)	Reaction time (days)	Surface area (m ² /g)
0.25	0.22	6	47.2
0.33	0.27	3	68.3
0.4	0.24	3	63
0.4	0.28	6	38

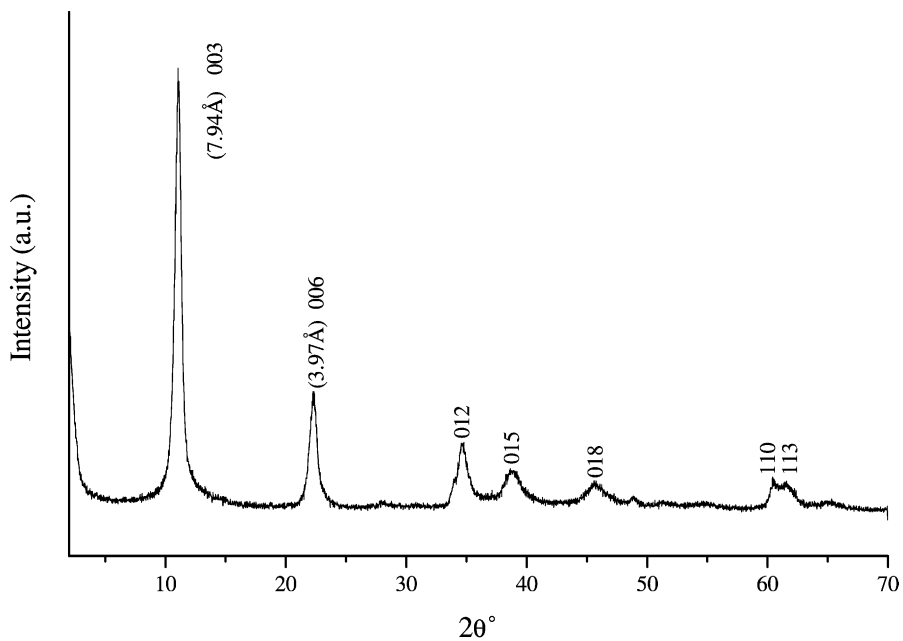


Fig. 1. XRPD diffraction patterns of $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135} \cdot 0.58\text{H}_2\text{O}$.

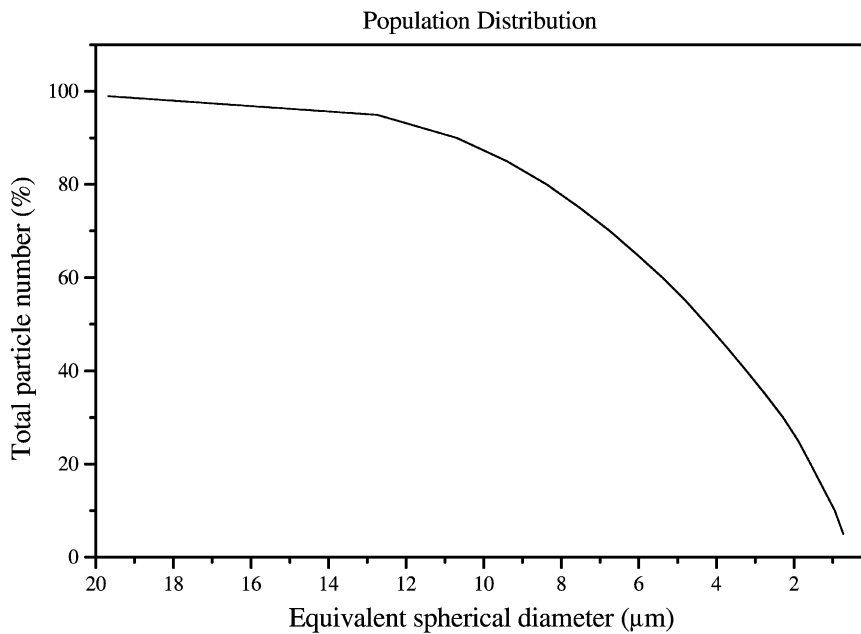


Fig. 2. Cumulative particle size distribution of the microcrystals of $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135} \cdot 0.58\text{H}_2\text{O}$.

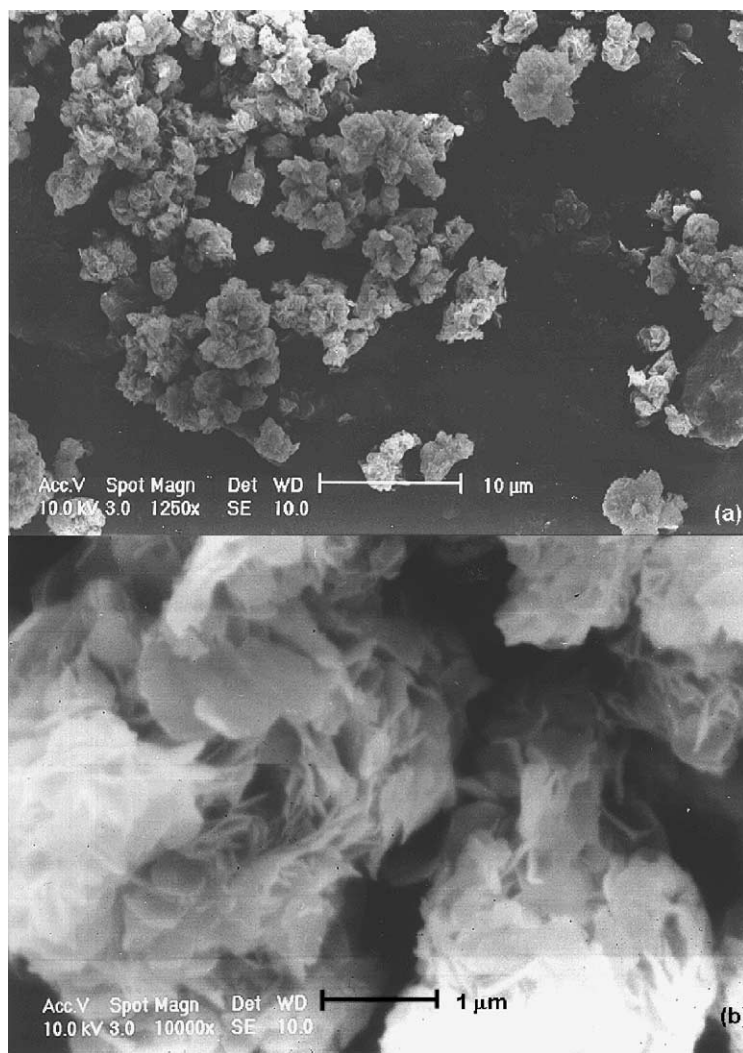


Fig. 3. SEM micrographs of $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135}\cdot 0.58\text{H}_2\text{O}$ microcrystals.

sharp endothermic effect [6]. The XRPD pattern of the sample heated at 1000°C showed the typical reflections of NiO and of NiAl_2O_4 . On the basis of the weight loss curve and of chemical analyses, the sample was found to have the following empirical formula: $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135}\cdot 0.58\text{H}_2\text{O}$. Attempts have been made to estimate the base strength of the surface sites by means of the indicator method [28], as described in the Section 2. It has been found that Bromotymol-blue ($\text{p}K_{\text{a}} = 7.1$), phenolphthalein ($\text{p}K_{\text{a}} = 9.6$) and brilliant cresyl blue ($\text{p}K_{\text{a}} = 11$), adsorbed on the surface of the solid, assume the colour

of the base form, while adsorbed tropaeolin ($\text{p}K_{\text{a}} = 11.8$) assumes the colour of the acid form. These observations let to conclude that the $\text{NiAl}-\text{CO}_3$ possesses basic sites with $\text{p}K_{\text{a}}$ values in the 11–11.8 range. These values are very similar to the $\text{p}K_{\text{a}2}$ of carbonic acid, indicating that the basic sites are the charge balancing carbonate anions. It should be noted that calcined $\text{MgAl}-\text{CO}_3$ shows basic sites with $\text{p}K_{\text{a}}$ values up to 16.5 [24].

At the end of the characterisation it may be concluded that the catalyst has empirical formula $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135}\cdot 0.58\text{H}_2\text{O}$, it consists

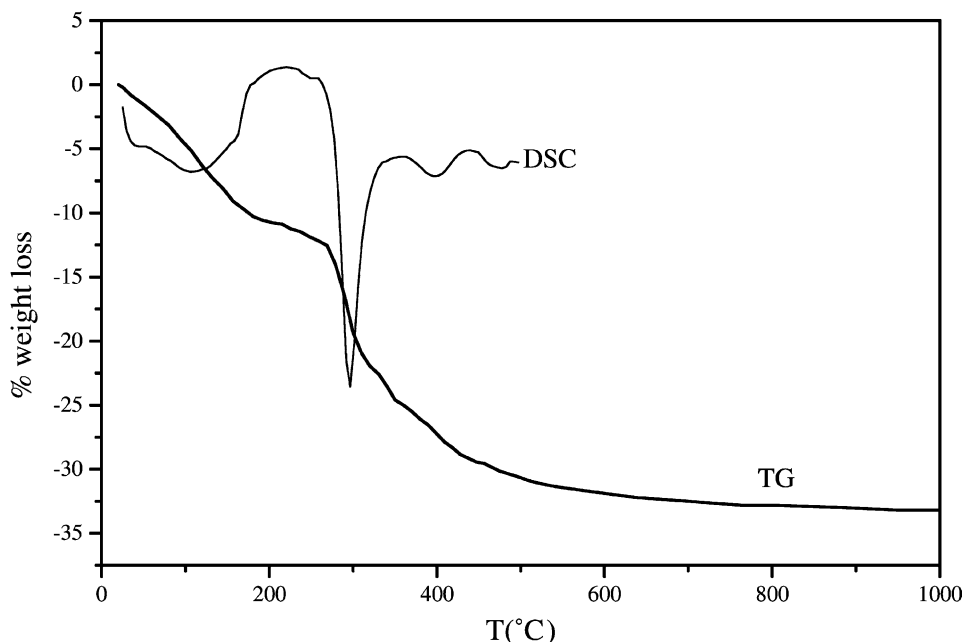
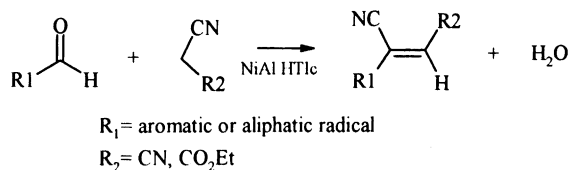


Fig. 4. Weight loss and DSC curves of $[\text{Ni}_{0.73}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3)_{0.135}\cdot 0.58\text{H}_2\text{O}]$. Heating rate $2^\circ\text{C}/\text{min}$, air-flow $30\text{ ml}/\text{min}$.

of aggregates of thin platelets with dimensions ranging from 0.5 to $10\ \mu\text{m}$ and has a specific surface area of $68.3\text{ m}^2/\text{g}$. The material loses hydration water at 150°C and possesses basic sites with $\text{p}K_a$ values up to 11.8 .

3.2. Catalytic activity

Preliminary experiments showed that NiAl-CO_3 catalyses the Knoevenagel reactions, that is:



It may be observed that the substrates ($\text{R}_2 = \text{CN}$, CO_2Et) have acidic methylene groups with $\text{p}K_a$ near to 9 and 11 , respectively and they may be deprotonated by the catalyst to generate the corresponding carbanion, able to attack an electron acceptor centre. It has been found that the catalyst is not able to pull off protons from dimethyl malonate ($\text{p}K_a = 13$) and Knoeve-

nagel adducts with this substrate were not obtained. This observation is a further support that the catalyst has surface basic sites with $\text{p}K_a$ lower than 11.8 .

Table 2 reports the reaction time and the yield of several reactions performed with substrates having $\text{R}_2 = \text{CN}$ or CO_2Et and R_1 an aliphatic or aromatic radical. All the reactions (see Section 2) were carried out at 60°C in solvent-free condition by adding the aldehyde to a well stirred mixture of the active methylene derivatives and catalyst NiAl HTlc , previously treated at 150° for 1 h . Aliphatic and aromatic aldehydes react in a short time and the Knoevenagel adducts were obtained in good to excellent yield. The high yields obtained may be also due to the presence of the anhydrous catalyst that is able to co-intercalate water molecules generated in the Knoevenagel condensation (see scheme) and withdraw the reaction equilibrium to the formation of the adduct. It has been indeed found that anhydrous $\text{NiAlCO}_3\text{ HTlc}$, recovered at the end of the reaction between benzaldehyde and malononitrile (see Table 2, entry 1) and washed with anhydrous CH_2Cl_2 contained about $0.6\text{ mol H}_2\text{O}/\text{mol}$.

Note that the amount of water generated by the various condensation reactions is generally higher than

Table 2

Knoevenagel condensation of aldehydes with ethylcyanoacetate and malononitrile, carried out at 60 °C in solvent-free conditions

Entry	Aldehyde	Ethylcyanoacetate		Malononitrile	
		Time (h)	Yield ^a (%)	Time (h)	Yield ^a (%)
1	Benzaldehyde	24	35 ^b	0.5	97 ^b
2	4-Hydroxy-3-methoxybenzaldehyde	5	74	1	70
3	3-Hydroxy-4-methoxybenzaldehyde	7	92	24	84
4	4-Methylbenzaldehyde	24	53	1	93
5	2-Methylbenzaldehyde	5	76 ^b	1	96 ^b
6	4-Methoxybenzaldehyde	6	70 ^b	1.5	84 ^b
7	Salicylaldehyde	24	79	4	53
8	3-Phenylprop-2-enal	24	82 ^b	1	93 ^b
9	Cyclohexanecarbaldehyde	5	80 ^b	3	83 ^b
10	Hexanal	1	60 ^b	0.5	95 ^b

The 1 mmol of substrates and 50 mg of catalyst.

^a Determined by ¹H NMR analysis.^b ¹H NMR data are reported in ref. [21].

that the catalyst is able to take up. However, the slight excess of water seems not to influence the performance of the catalyst. The condensation of benzaldehyde with malononitrile, carried out in the same conditions of Table 2, but in the presence of not anhydrous acetonitrile, as solvent, occurred in longer time (3 h) but with comparable yields (90%).

It is important to note that in the case of α,β -unsaturated aldehydes the reaction occurs without formation of the Michael-type addition adduct (Table 2, entry 8). When ethylcyanoacetate was used as active methylene compound the reaction occurred with the stereoselective formation of *E* configured olefins. For example, in the case of the adduct obtained from 4-methoxy benzaldehyde and ethylcyanoacetate (entry 6) a small NOE effect was detected between the

olefinic proton and the methylene of the carboethoxy group [29].

This result clearly demonstrated that this solid base catalyst is a practical alternative to soluble bases in Knoevenagel condensation with the following advantages: (a) high catalytic activity, (b) solvent-free condition, (c) mild reaction condition, (d) simple work-up, (e) use of no toxic and inexpensive catalyst, (f) recyclable nature of catalyst [30]. The catalyst washed with dichloromethane and dried at 150° can be reused for several experiments. The reaction in entry 4 has been repeated three times with the following yields: 93, 91, 90%.

Moreover, it seemed of interest to compare the results obtained in this study with some of those reported in the literature for the Knoevenagel

Table 3

Comparison of reaction yield and reaction time of Knoevenagel condensation of aldehydes (see entries 1 and 8 of Table 2) and malononitrile in the presence of the listed catalysts

Catalyst	Entry 1		Entry 8	
	Time (h)	Yield (%)	Time (h)	Yield (%)
NiAlCO ₃ (this work)	0.5	97	1	93
α -Zr(KPO ₄) ₂ [21]	0.2	92	0.2	89
Zeolite [32]	12 ^a	78	8	70
Modified amberlite IRC-50 [33]	5 ^a	92	5 ^a	65
MgAl-O- <i>t</i> -Bu [34]	0.16 ^a	99		
Calcined MgAl, water vapour activated [35]	1 ^{a,b}	100		

^a Reaction carried out at room temperature.^b Reaction carried out in toluene.

condensation catalysed by other base catalysts. For this purpose the reactions with malononitrile (entries 1 and 8) have been taken into consideration and the data are compared in Table 3. In general, the use of the catalyst NiAl HTlc allows to achieve excellent yields in short reaction time. The catalyst Mg-Al-O-*t*-Bu and the catalyst consisting of calcined MgAl HTlc, activated by water vapor, show a better activity, but their preparation is more complex and their stability lower than those of NiAl HTlc since they suffer from CO₂ contamination. The use of α -Zr(KPO₄)₂, permits to achieve yields similar to those obtained with NiAl HTlc but in shorter time, however, the use of HTlc is preferable because it is of simpler preparation and more inexpensive than α -Zr(KPO₄)₂.

4. Conclusion

Ni–Al hydrotalcite-like compounds in carbonate form possess sites with base strength sensibly lower than that of the mixed oxides obtained by thermal decomposition. However, as already observed by Constantino and Pinnavaia [31], the basic properties of HTlc are enhanced as a consequence of the dehydration at temperatures ($\leq 250^\circ\text{C}$), lower than those of thermal de-carbonatation. The NiAl–CO₃, used in the present study, showed a sufficiently high base strength to catalyse Knoevenagel condensation of aldehydes with malononitrile and ethylcyanoacetate but not with dimethylmalonate. This implies that synthetic hydrotalcites as such may be used in liquid phase organic synthesis and also selective reactions may be conceived.

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