

*Dedicated to Professor Claude Nicolau  
 on the occasion of his 80th anniversary*

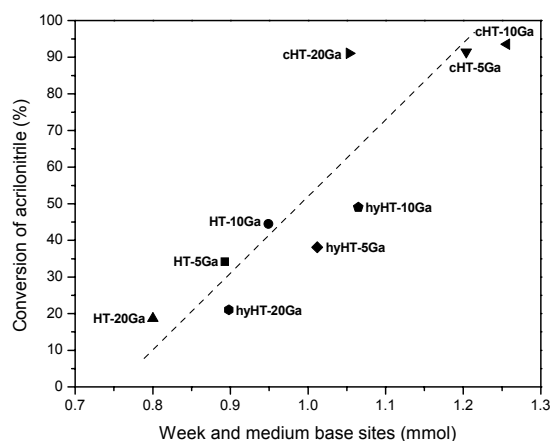
## THE EFFECT OF MODIFYING CATIONS ON THE CATALYTIC ACTIVITY OF HYDROTALCITE-LIKE COMPOUNDS IN 1,4-ADDITION REACTIONS

Octavian Dumitru PAVEL, Rodica ZĂVOIANU\* and Emilian ANGELESCU

University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis,  
 4-12 Regina Elisabeta Av., 030018, Bucharest, Roumania

Received November 17, 2015

The influence of the modifying cations on the catalytic activity of hydrotalcite-like compounds in 1,4-addition of ethanol to acrylonitrile has been investigated. This type of reaction is peculiarly sensitive to the basicity of the catalyst. The modification of hydrotalcite  $Mg_{0.75}Al_{0.25}$  with cations having higher electronegativity than that of Mg (1.2) and Al (1.5), such as Ga (1.6), Fe (1.8) and Cu (1.9), induced different base sites distributions in the modified hydrotalcite-like structures. Calcination of these materials followed by reconstruction, via memory effect, also plays an important role in modifying the basicity. This modification of basicity leads to a change in the catalytic activity for 1,4-addition of ethanol to acrylonitrile. Due to the presence of Jahn-Teller effect (the distortion in the octahedral coordination structure which leads to a gain in energy) in case of Cu-modified hydrotalcite the activity is higher than it would be expected. For all catalysts, there is a total selectivity toward the main reaction product, namely *beta*-ethoxypropionitrile.



### INTRODUCTION

The last two decades brought an increased interest for the investigation of solid base catalysts as an alternative to soluble base catalysts which have a corrosive action and are harmful to the environment. Among the solid bases, the class of layered double hydroxides (LDH) and their corresponding mixed oxides plays an important part.<sup>1-8</sup> An issue that hindered their investigation was their affinity for the adsorption of  $CO_2$  from the atmosphere compared with acid materials

which were stable under air. LDH consist of brucite-like layers having positive charge with anionic species in the interlayer, forming neutral materials with the general formula:  $[M^{2+}_x M^{3+}_{1-x} (OH)_2]^{x+} [A^{n-}_{x/n}] \cdot mH_2O$  where  $M^{2+}$  and  $M^{3+}$  are divalent and, trivalent metals, respectively  $A^{n-}$  is an anion and  $x$  can have values between 0.2-0.33.<sup>2</sup> When  $M^{2+}$  is  $Mg^{2+}$ ,  $M^{3+}$  is  $Al^{3+}$  and  $A^{n-}$  is  $CO_3^{2-}$ , the LDH compound is called hydrotalcite (HT). Hydrotalcite are known to display a "memory effect", namely the possibility to reconstruct their initial structure when the mixed

\* Corresponding author: rodica.zavoianu@g.unibuc.ro

oxides obtained by calcination of HT parents up to 600°C are contacted with an aqueous solution containing different anions.<sup>2,9,10</sup> Both Mg<sup>2+</sup> and Al<sup>3+</sup> may undergo isomorphic substitution with other elements (usually the elements with cationic radius close to Mg<sup>2+</sup>=0.72 Å or Al<sup>3+</sup>= 0.535 Å) which can be accommodated in the holes of the close packed configuration of OH groups in the brucite-like layers.<sup>2</sup>

The electronegativity of the modifying cations plays an important role in creating sites with different base strength. Thus, a lower electronegativity value increases the basic character, while a higher value has an opposite effect.

One of the important reactions in organic chemistry is the 1,4-addition of ethanol to acrylonitrile which usually takes place with high selectivity in the presence of base catalysts yielding *beta*-ethoxypropionitrile. This reaction, also called “cyanoethylation”,<sup>11</sup> is a commercial route for the manufacture of pharmaceuticals or paints, or it can be followed by hydrogenation to synthesize functionalized primary amines.<sup>12-15</sup> This reaction is not hindered by CO<sub>2</sub> adsorption at room temperature because the alcohols are adsorbed much faster and stronger on the base sites compared to CO<sub>2</sub>.<sup>16</sup>

Since the literature lacks conclusive information regarding the influence of the modifiers on the catalytic activity of HTlc compounds for 1,4-addition reactions, this paper aims to bring new insights on this aspect. The modifier elements which will be taken into account are gallium, iron and copper at different concentrations. All these elements have a higher electronegativity than Mg (1.2) and Al (1.5), *e.g.* Ga (1.6), Fe (1.8) and Cu (1.9), respectively. Taking into account that the ionic radii for Ga<sup>3+</sup> (0.62Å) and Fe<sup>3+</sup> (0.645Å) are fairly close to that of Al<sup>3+</sup> (0.535 Å) and the ionic radius of Cu<sup>2+</sup> (0.73Å) is almost equal to that of Mg<sup>2+</sup> (0.72Å), it may be expected that these elements would be able to substitute Al<sup>3+</sup> and Mg<sup>2+</sup> in the hydrotalcite-like crystallographic structure. Based on these facts, it would be expected that the differences in the catalytic activities of the modified HTlc and the parent HT would be related mostly to the differences in the base sites strength distribution.

## EXPERIMENTAL

### 1. Catalysts preparation

A standard hydrotalcite with Mg/Al=3 molar ratio can be obtained by co-precipitation under low super-saturation conditions<sup>17</sup> at pH 10 using a 1.5 M nitrate solution (A) containing the appropriate amounts of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck reagents p.a.) solved in bi-distilled water and a mixture of NaOH and Na<sub>2</sub>CO<sub>3</sub> (concentration 1 M Na<sub>2</sub>CO<sub>3</sub>) as adjusting pH solution (B). Both solutions were mixed at room temperature under vigorous stirring, (600 rot·min<sup>-1</sup>), at a feeding flow of 60 mL·h<sup>-1</sup>. The gel obtained was aged 18 h at 75 °C, cooled to room temperature, filtered and washed with *bi*-distilled water until neutral pH 7 was reached. The drying of the hydrotalcite gel was performed at 90 °C for 24 h in air flow, yielding HT solid. For the preparation of modified samples part of magnesium or aluminum nitrates were replaced by gallium, iron and copper nitrate in different amounts, in order to obtain solids with different concentrations of the modifier *e.g.* 5, 10 and 20 wt%, respectively. The HTlc obtained by isomorphic exchange were abbreviated as HT-5(M), HT-10(M), HT-20(M) where M = Ga, Fe and Cu. All parent samples were calcined at 460°C during 18 h; yielding the mixed oxide samples: CHT-5(M), CHT-10(M), CHT-20(M). Reconstructions of the HTlc structures were carried out at room temperature by contacting the above mentioned mixed oxides with *bi*-distilled water during 24 h followed by drying at 90 °C for 24 h in air flow. The resulted solids were abbreviated as: hy-HT5(M), hy-HT10(M), hy-HT20(M).

### 2. Catalysts characterization

The catalysts were characterized by chemical and elemental analysis. The determination of the metal content was performed by Atomic Absorption Spectrometry on Pye-Unicam AAS Spectrometer. N, H and C were determined by elemental analysis on Carlo Erba automatic analyzer.

Powder X-ray diffraction patterns were recorded with a Shimadzu XRD 7000 diffractometer using Cu K<sub>α</sub> radiation (λ = 1.5418 Å, 40 kV, 40 mA) at a scanning speed of 0.10° min<sup>-1</sup> in the 5 – 80° 2 theta range.

DRIFTS spectra obtained from accumulation of 600 scans in the domain 400 – 4000 cm<sup>-1</sup> were recorded with NICOLET 4700 spectrometer.

One of the most popular techniques for the determination of the base sites in a solid is the thermo-programmed desorption of carbon dioxide, CO<sub>2</sub>-TPD. However, this technique can be applied only for the determination of the base sites in oxide materials since the structure of the parent HT would be destroyed when the desorption of CO<sub>2</sub> is carried out by heating the samples up to 700°C. Therefore, it is more appropriate to compare the basicity of dried and calcined samples using the irreversible adsorption of organic acids with different pK<sub>a</sub> under ambient conditions. According to this technique, acrylic acid, pK<sub>a</sub> = 4.2, is utilized to determine the total number of base sites, and phenol, pK<sub>a</sub> = 9.9 is utilized to determine the number of strong base sites.<sup>17-20</sup> The number of weak and medium base sites is given by the difference between the amounts of adsorbed acrylic acid and phenol.

### 3. Catalytic tests

In a typical procedure for the 1,4-addition of ethanol to acrylonitrile, the ethanol (0.03 mmol) and acrylonitrile (0.01 mmol) are poured in a reactor equipped with a reflux condenser, mixed at 600 rot·min<sup>-1</sup> and heated on a silicon oil bath up to the reflux temperature when the catalyst (3% w/w) was added. Hourly, during a 5 h reaction time, 50 μL were extracted and analyzed by G.C. using a K072320 Termo-Quest chromatograph equipped with a FID detector and a capillary column of 30 m length and 0.324 mm diameter and DB-5 stationary phase. Highly pure N<sub>2</sub> (99.999%) was used as carrier gas.

## RESULTS AND DISCUSSION

The chemical compositions of modified hydrotalcite-like structures are shown in Table 1.

Only HT-20Fe and HT-20Ga correspond for HTlc in which aluminum was totally substituted by Fe<sup>3+</sup> and Ga<sup>3+</sup>. Except for HT-20Fe all the other structures respect a molar ratio of 3 between the bivalent and trivalent cations. Cu<sup>2+</sup> does not substitute completely Mg<sup>2+</sup> from the brucite-type layer.

The XRD patterns, Fig. 1A, present the typical lines for layered double hydroxides for all samples with sharp and symmetric reflections for **003**, **006**, **110**, **113** planes and broad asymmetric lines for **012**, **015**, **018** planes (JCPDS 70-2151). The cell parameters, Table 2, are given by  $a = 2 \cdot d_{110}$  and  $c = 3/2 \cdot (d_{003} + 2d_{006})$ , respectively. The interlayer space for parent materials is approximately the same. For Cu modified hydrotalcites, the crystallite size decreases sharply due to the cations which were not accommodated in octahedral positions. This could be a consequence of the fact that Cu<sup>2+</sup> ions are more stable in tetrahedral positions. Even

IFS parameter decreases with the amount of the modifier cation, the  $a$  parameter does not suffer significant changes because the substitution of cations from the hydrotalcite structure is made with cations having the appropriate radius: Mg<sup>2+</sup>=0.72Å with Cu<sup>2+</sup>=0.73Å; and Al<sup>3+</sup>=0.535Å with Fe<sup>3+</sup>=0.645Å and Ga<sup>3+</sup>=0.62Å. The XRD patterns evidence the formation of a (Mg/M<sup>2+</sup>)(Al<sup>3+</sup>/M<sup>3+</sup>)O solid solution of MgO-periclase type (JCPDS-45-0946).<sup>2,21</sup> The sample modified with 20% Cu shows the diffraction lines corresponding to CuO phase which is stable even after reconstruction of LDH structure, Fig. 1C. The XRD patterns of the reconstructed samples Fig. 1C, show that reconstruction did not change significantly the  $a$  parameter, but in case of  $c$  parameter for Ga and Fe modified samples, there is a decreasing trend due to a partial replacement of CO<sub>3</sub><sup>2-</sup> from interlayer with OH<sup>-</sup> which has lower ionic radius. For hy-HT10Cu and hy-HT20Cu there is a light increase of  $c$  parameter due to presence of Jahn-Teller effect. The XRD patterns in Fig. 1B, show that calcination of parent samples, leads to obtaining of mixed oxides type materials.

Table 1

Chemical composition of parent samples

Samples	Weight composition (%)						Molar ratio	Molar ratio	Molar ratio
	Mg	Al	Cu	Ga	Fe	C	Mg <sup>2+</sup> /Cu <sup>2+</sup>	Al <sup>3+</sup> /M <sup>3+</sup>	M <sup>2+</sup> /M <sup>3+</sup>
HT-5Ga	23.42	6.76	-	4.93	-	1.93	-	3.6	3.01
HT-10Ga	22.71	4.62	-	9.77	-	1.87	-	1.2	3.00
HT-20Ga	21.16	-	-	20.23	-	1.74	-	0.0	3.00
HT-5Fe	23.52	6.27	-	-	5.04	1.94	-	2.4	2.94
HT-10Fe	22.88	3.56	-	-	10.16	1.88	-	0.7	3.00
HT-20Fe	20.91	-	-	-	19.99	1.72	-	0.0	2.41
HT-5Cu	21.44	8.66	5.10	-	-	1.92	11.0	-	3.00
HT-10Cu	18.90	8.40	9.88	-	-	1.87	5.0	-	3.00
HT-20Cu	13.38	7.82	20.26	-	-	1.74	1.7	-	3.00

Table 2

Lattice parameters and structural characteristics of the investigated samples

Samples	$a$ (Å)	$c$ (Å)	IFS* (Å)	FWHM 003 <sup>(a)</sup> /200 <sup>(b)</sup>	D-cryst. size 003(Å) <sup>(a)</sup> /200(Å) <sup>(b)</sup>
HT	3.069	23.643	3.08	0.912	88
HT-5Ga	3.0547	22.9553	2.8518	0.5185	153.94
HT-10Ga	3.0633	23.1140	2.9047	0.6633	120.33
HT-20Ga	3.0641	23.1138	2.9046	0.5747	138.88
HT-5Fe	3.0581	23.0121	2.8707	0.5427	147.08
HT-10Fe	3.0652	23.1571	2.9190	0.5252	151.96
HT-20Fe	3.0644	22.9986	2.8662	0.5472	145.87
HT-5Cu	3.0554	22.9869	2.8623	0.5523	144.52
HT-10Cu	3.0601	23.0086	2.8695	1.2041	66.29
HT-20Cu	3.0585	22.7877	2.7959	0.9689	82.39
cHT-5Ga	4.17	-	-	2.3900	164.80
cHT-10Ga	4.18	-	-	2.3600	128.77

Table 2(continued)

cHT-20Ga	4.18	-	-	2.2900	148.66
cHT-5Fe	4.17	-	-	2.3400	157.44
cHT-10Fe	4.18	-	-	2.1520	162.66
cHT-20Fe	4.18	-	-	2.2300	156.14
cHT-5Cu	4.17	-	-	2.4267	154.72
cHT-10Cu	4.18	-	-	2.6050	70.95
cHT-20Cu	4.16	-	-	2.3467	88.22
hy-HT-5Ga	3.0522	22.7844	2.7948	0.9254	86.26
hy-HT-10Ga	3.0630	23.1964	2.9321	0.7440	107.27
hy-HT-20Ga	3.0556	22.8642	2.8214	0.8932	89.37
hy-HT-5Fe	3.0542	22.8366	2.8122	0.9008	88.62
hy-HT-10Fe	3.0599	22.9905	2.8635	0.9315	85.69
hy-HT-20Fe	3.0615	22.9422	2.8474	0.9017	88.52
hy-HT-5Cu	3.0532	22.9428	2.8476	0.8785	90.86
hy-HT-10Cu	3.0610	23.2073	2.9358	0.8327	95.84
hy-HT-20Cu	3.0498	22.8700	2.8233	0.7506	106.35

\*IFS represent the interlayer free distance;

(a) corresponds to HTlc-phases;

(b) corresponds to the mixed oxides phases

The DRIFT spectra of parent samples, Fig. 2A, present the band corresponding to vibrations of hydroxyl and carbonate anions. Between 3700-3400  $\text{cm}^{-1}$  there is a band corresponding to OH group vibration,  $\nu(\text{O-H})$ , in the LDH structure and another band at 3070  $\text{cm}^{-1}$  corresponding to hydrogen bonding between water and carbonate in the interlayer space. The band at 1650  $\text{cm}^{-1}$  is due to  $\text{H}_2\text{O}$  bending vibration of interlayer water in the LDH structure. The bands at 1400  $\text{cm}^{-1}$  are assigned to  $\text{CO}_3^{2-}$  group vibrations in the LDH. In the region 1200-700  $\text{cm}^{-1}$  the spectra show bands characteristic to carbonates. During calcination process part of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  groups are removed from the structure therefore in the DRIFT spectra there is a decreased intensity of the bands at 3070  $\text{cm}^{-1}$  and 1650  $\text{cm}^{-1}$ , Fig. 2B. The maintaining of intense bands in the carbonate zone is explained by the fact that carbonate anions are not completely removed at the calcination temperature of 460  $^\circ\text{C}$ . According to literature data<sup>2</sup> carbonate is totally removed from the HTlc structure beyond 650 $^\circ\text{C}$ . The DRIFT spectra of the samples obtained by reconstruction, Fig. 2C, show a more pronounced incorporation of hydroxyl groups in the structure expressed by a higher intensity of the bands in the region 3600-3000  $\text{cm}^{-1}$ .

The base sites distribution results presented in Table 3 show that in all investigated solids the weak and medium strength base sites are prevailing over the strong base sites. Compared to their parents, all the calcined and hydrated samples have a higher number of strong base sites.

The results of the catalytic activity tests on the investigated samples are presented in Fig. 3. For all the catalysts the conversion of acrylonitrile increases with the reaction time and the calcined samples are more active than the hydrated or the parent samples (cHT>hyHT> HT). For the samples with 10 % wt. of modifier loading the increase of acrylonitrile conversion vs. time is faster than for the samples with 5 or 20 % wt. of modifier loading. According to the data in Table 3, these samples have also the highest proportion of weak and medium strength base sites. Ga-modified samples have higher activity than Fe modified samples. This fact could be related to the assumption that due to the lower electronegativity of Ga there is an increase of the basicities of Ga-containing solids compared to those of the samples modified with the same concentration of Fe. However, at least apparently this assumption lacks validity in what concerns Cu-modified samples which should be even less basic than Fe-modified ones. An answer to this issue can be suggested looking at the data presented in Table 1, where one can see that all three concentrations of  $\text{Cu}^{2+}$  lead to a  $\text{Mg}^{2+}/\text{Cu}^{2+}$  molar ratios higher than 1.7 while the molar ratio between bivalent and trivalent cations is 3, meaning there is always an excess of  $\text{Mg}^{2+}$  ions over  $\text{Cu}^{2+}$  and over  $\text{Al}^{3+}$  as well, and hence the increased basicities of Cu-containing samples compared to Ga and Fe-modified ones are explainable.

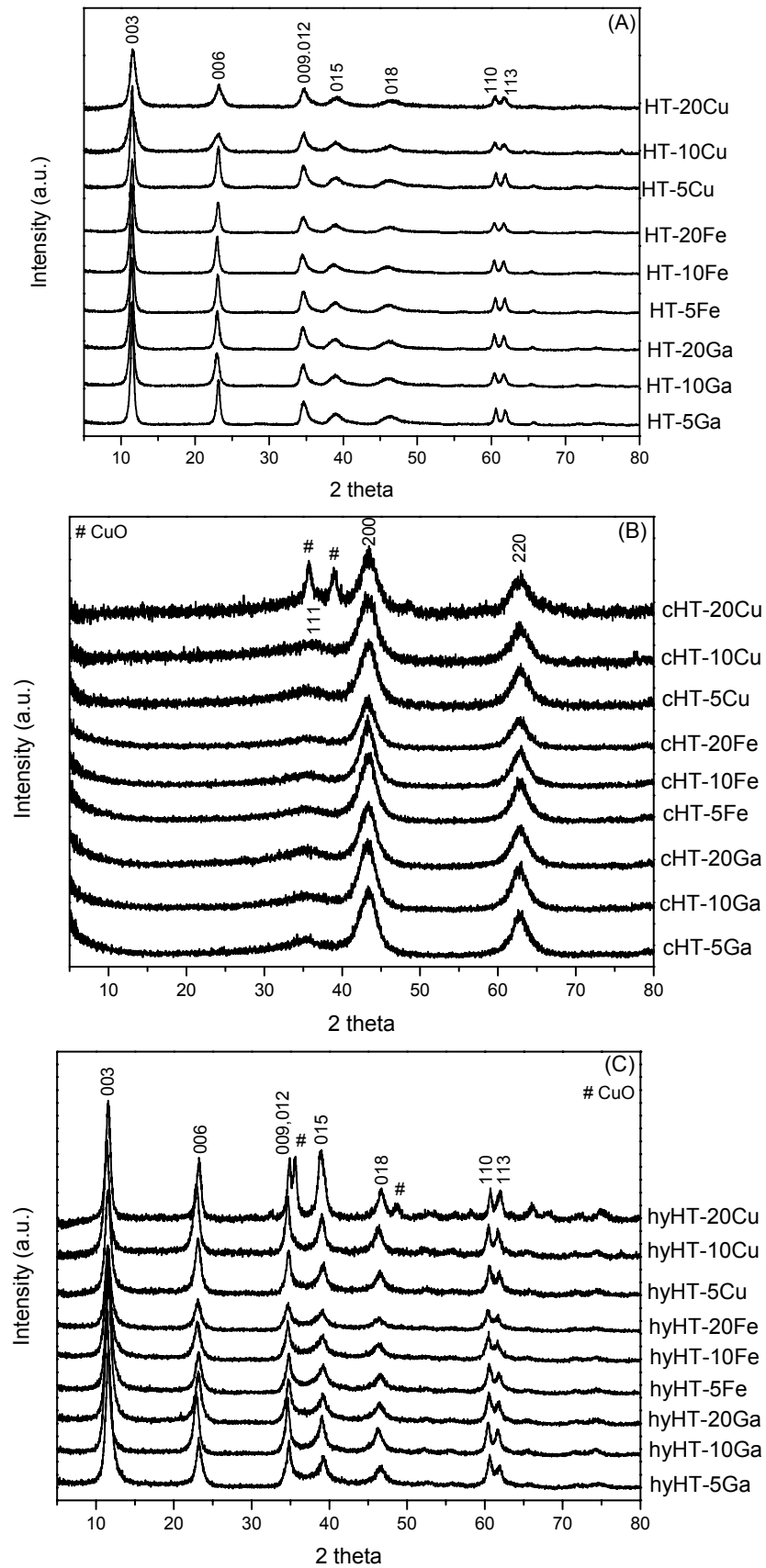


Fig. 1 – XRD Patterns of the investigated samples: (A) –HT-parents; (B) mixed oxides; (C) hydrated samples.

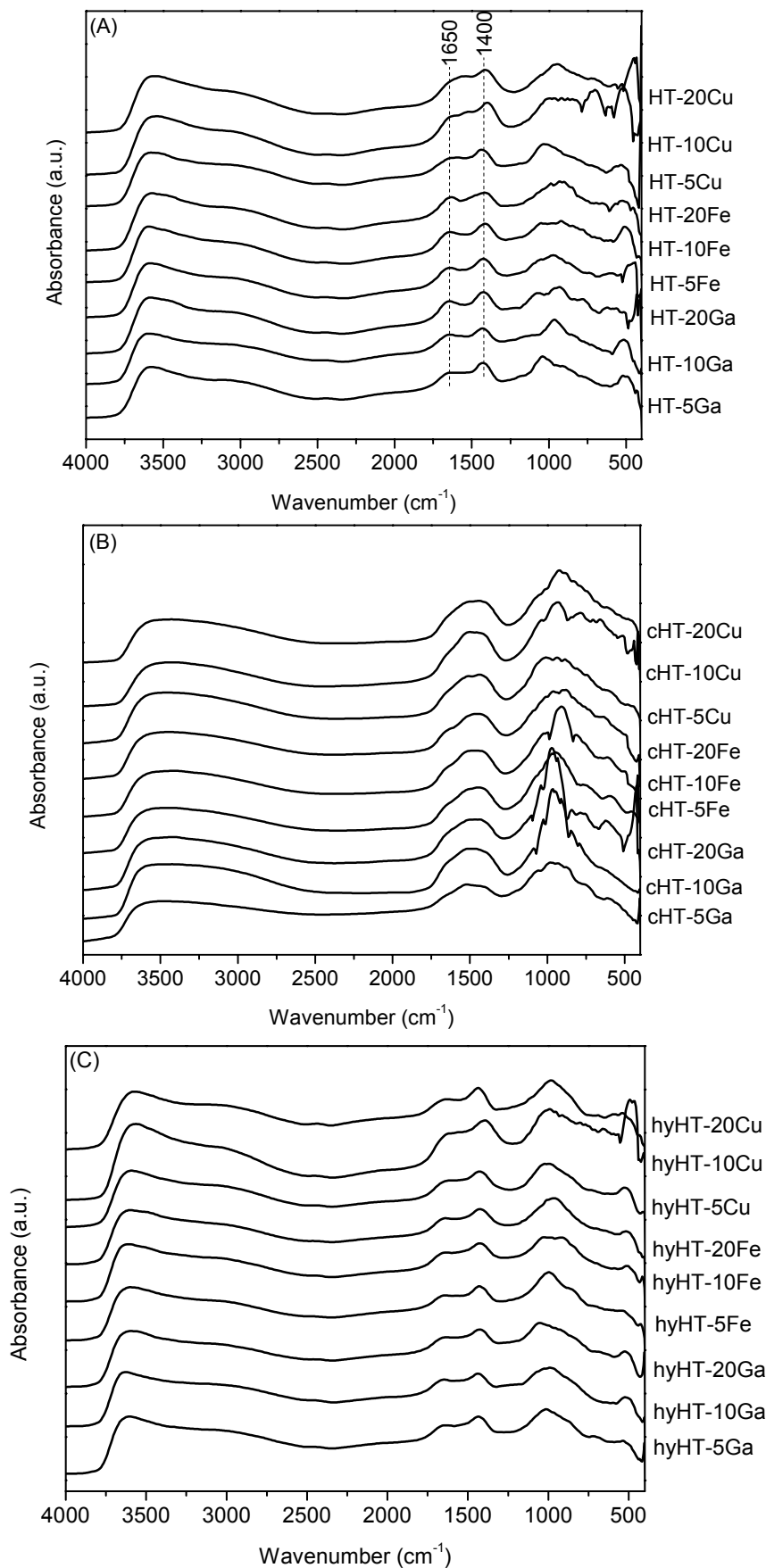


Fig. 2 – DRIFT spectra of the investigated samples: (A) –HT-parents; (B) mixed oxides; (C) hydrated samples.

Table 3

The base sites distribution for the investigated samples

Samples	Total number of base sites	Number of strong base sites	Weak and medium strength base sites (mmol/g)	% strong base sites	% weak and medium strength base sites
	mmol AA/g*	mmolPhOH/g <sup>#</sup>			
HT-5Ga	1.125	0.232	0.893	20.6	79.4
HT-10Ga	1.180	0.231	0.949	19.6	80.4
HT-20Ga	1.135	0.335	0.800	29.5	70.5
HT-5Fe	1.068	0.225	0.843	21.1	78.9
HT-10Fe	1.074	0.196	0.878	18.2	81.8
HT-20Fe	1.115	0.285	0.830	25.6	74.4
HT-5Cu	1.168	0.268	0.900	22.9	77.1
HT-10Cu	1.192	0.245	0.947	20.6	79.4
HT-20Cu	1.416	0.596	0.820	42.1	57.9
cHT-5Ga	1.730	0.526	1.204	30.4	69.6
cHT-10Ga	1.790	0.534	1.256	29.8	70.2
cHT-20Ga	1.629	0.576	1.053	35.4	64.6
cHT-5Fe	1.708	0.529	1.179	31.0	69.0
cHT-10Fe	1.670	0.504	1.166	30.2	69.8
cHT-20Fe	1.720	0.617	1.103	35.9	64.1
cHT-5Cu	1.733	0.524	1.209	30.2	69.8
cHT-10Cu	1.715	0.514	1.201	30.0	70.0
cHT-20Cu	1.858	0.668	1.190	36.0	64.0
hyHT-5Ga	1.345	0.333	1.012	24.8	75.2
hyHT-10Ga	1.365	0.300	1.065	22.0	78.0
hyHT-20Ga	1.282	0.384	0.898	30.0	70.0
hyHT-5Fe	1.430	0.485	0.945	33.9	66.1
hyHT-10Fe	1.272	0.301	0.971	23.7	76.3
hyHT-20Fe	1.505	0.593	0.912	39.4	60.6
hyHT-5Cu	1.338	0.337	1.001	25.2	74.8
hyHT-10Cu	1.306	0.286	1.020	21.9	78.1
hyHT-20Cu	1.615	0.695	0.920	43.0	57.0

\* AA – acrylic acid; # PhOH - phenol

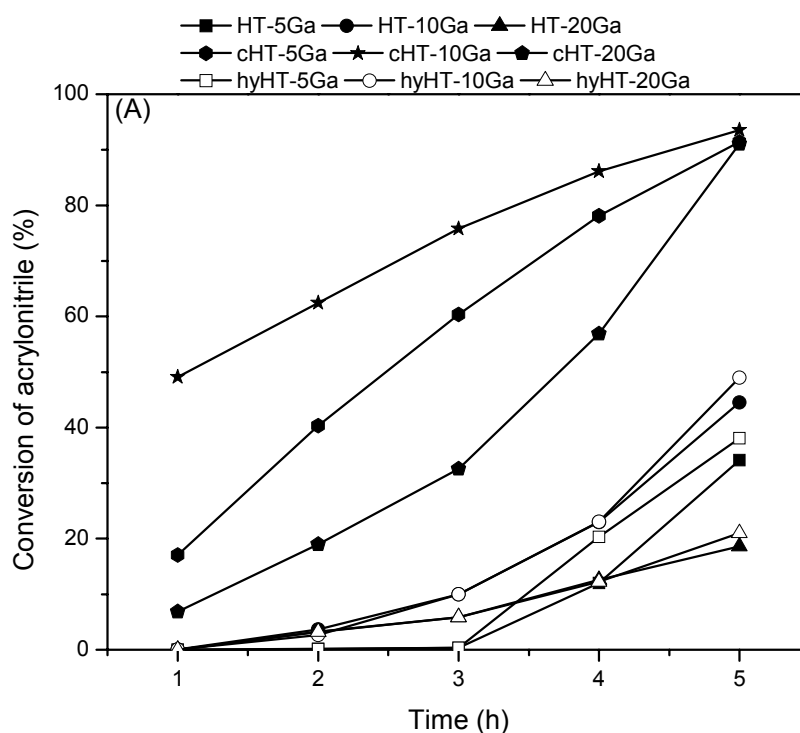


Fig. 3 – Variation of acrylonitrile conversion vs. reaction time (A) – Ga modified HTlc, (B) – Fe modified HTlc; (C) Cu modified HTlc.

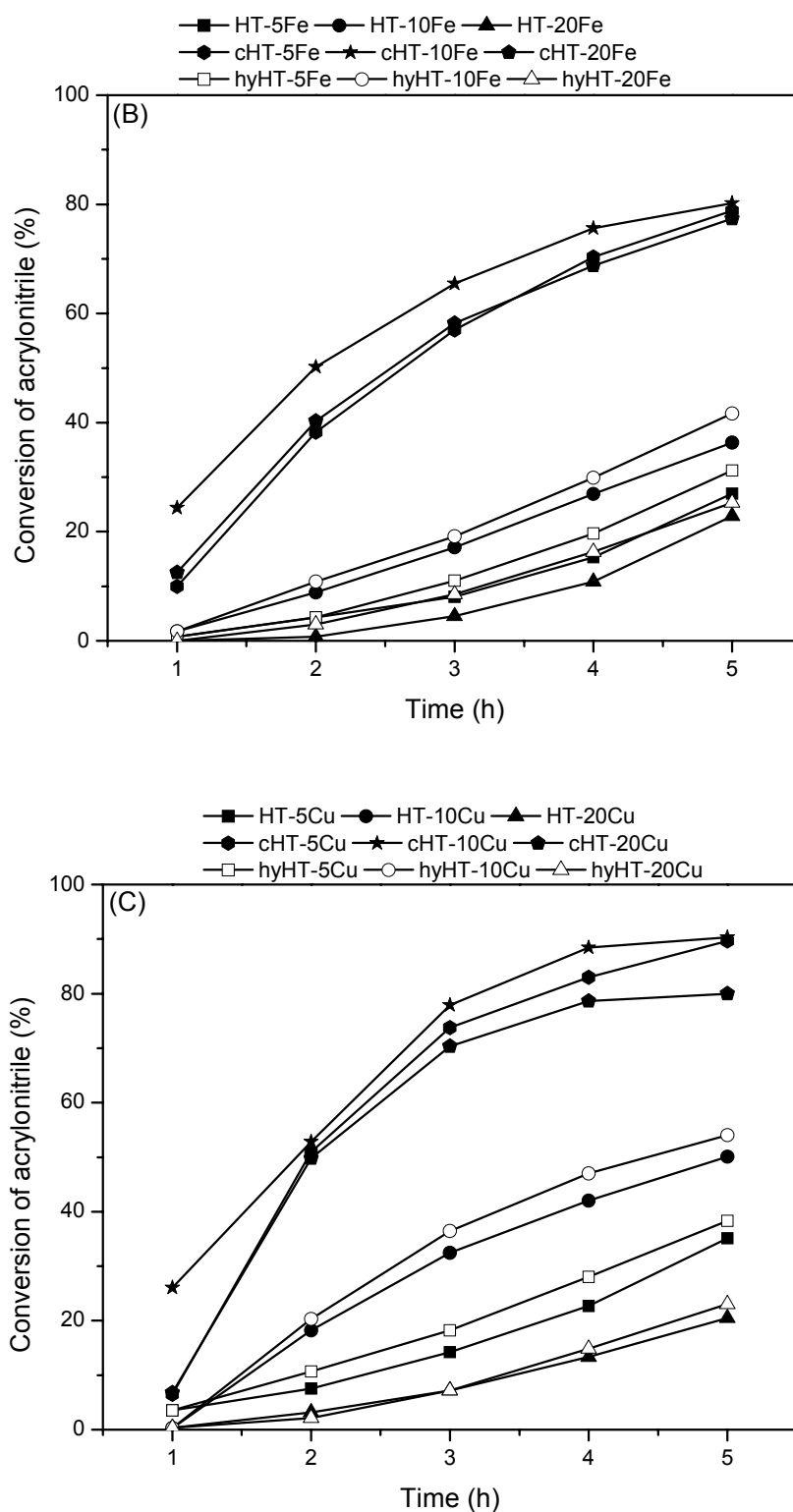


Fig. 3 (continued) – Variation of acrylonitrile conversion vs. reaction time (A) – Ga modified HTIc, (B) – Fe modified HTIc; (C) Cu modified HTIc.

As it may be seen from the data plotted in Fig. 4, for each series of solids there is a linear correlation between the number of weak and

medium strength base sites and the conversion of acrylonitrile after 5h reaction time, which is in agreement with literature data.<sup>12,17,21,22</sup>



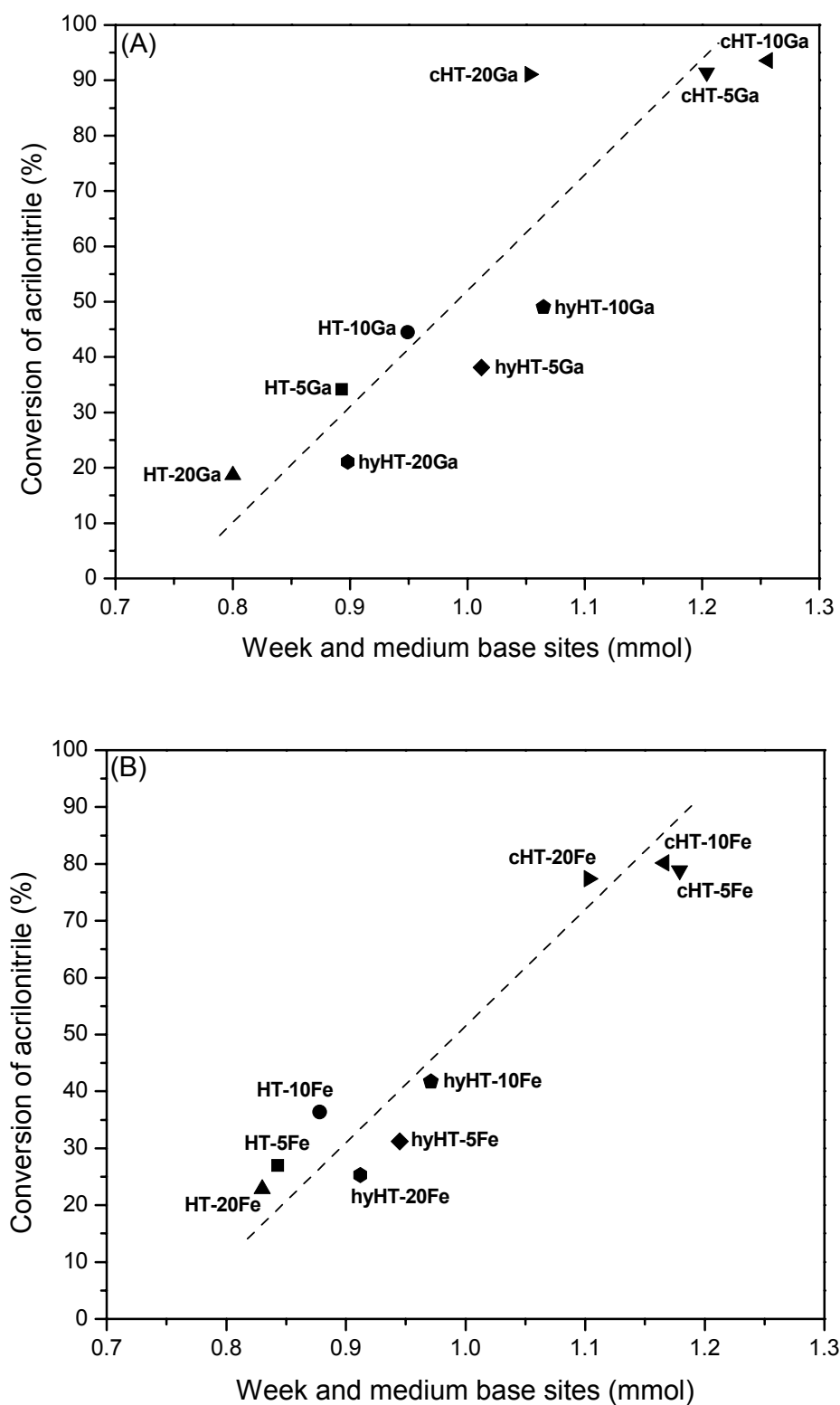


Fig. 4 (continued) – Linear trend dependence between the conversion of acrylonitrile after 5h reaction time and the number of weak and medium strength base sites of the samples.

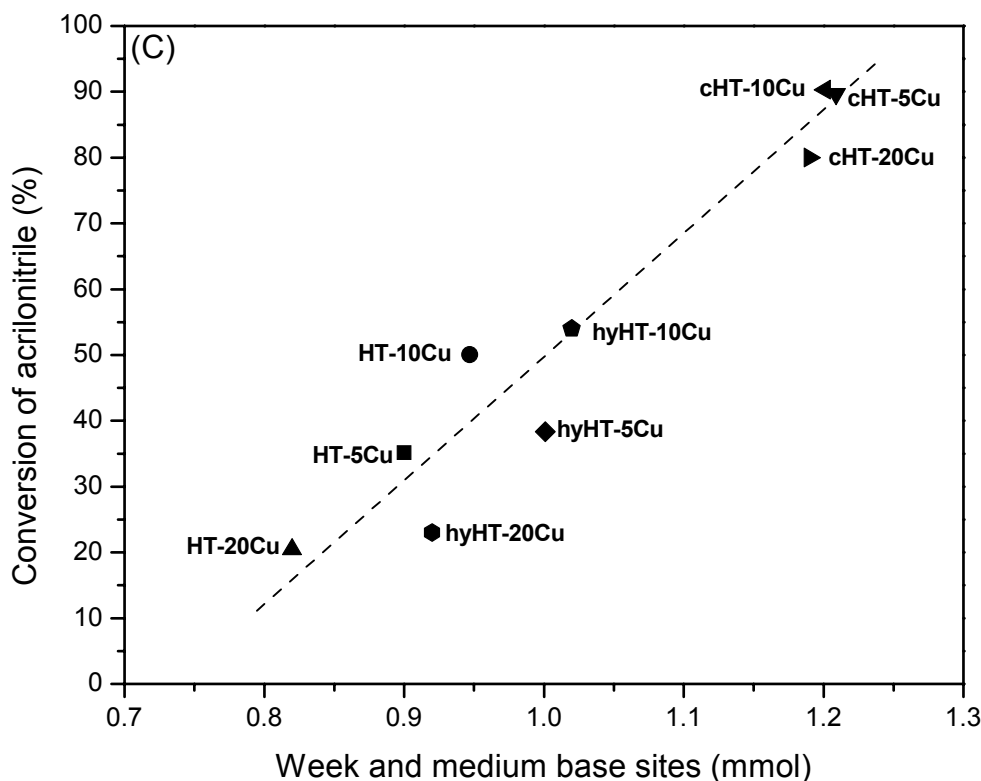


Fig. 4 – Linear trend dependence between the conversion of acrylonitrile after 5 h reaction time and the number of weak and medium strength base sites of the samples.

## CONCLUSIONS

Hydrotalcites modified with cations having increased electronegativity compared to  $Mg^{2+}$  or  $Al^{3+}$  can be prepared easily when the ionic radius of the modifier is similar to that of the cation bearing the same charge in the brucite-type layer. This affirmation is supported by the results obtained in XRD and DRIFT characterizations. All the samples exhibited the memory effect. However, in case of Cu modified samples, a distinct CuO phase is formed after calcinations, and this phase is preserved even after the reconstruction by hydration. There is a linear correlation between the sum of weak and medium strength base sites vs. conversion of acrylonitrile after 5 h reaction time. For each series of modified samples, the trend of activity is cHT>hyHT> HT.

The lower conversions are obtained for the samples where there is an excess of modifier having a higher electronegativity than the cation with equivalent charge in the reference hydrotalcite structure. In the case of Cu-modified samples, the Jahn-Teller effect characteristic to Cu could also play an important role in enhancing the catalytic activity of these samples.

*Acknowledgments:* This work was supported by UB grants 21/2013 and 272/2013.

## REFERENCES

1. A. Gil and L.M. Gandía, *Catal. Rev.*, **2000**, *42*, 145-212.
2. F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, **1991**, *11*, 173-301.
3. B. F. Sels, D.E. De Vos and P.A. Jacobs, *Catal. Rev.*, **2001**, *43*, 443-488.
4. Y. Ono and T. Baba, *Catal. Today*, **1997**, *38*, 321-337.
5. C. Li, M. Wei, D.G. Evans and X. Duan, *Catal. Today*, **2015**, *247*, 163-169.
6. F. Hamerski and M.L. Corazza, *Appl. Catal. A-Gen.*, **2014**, *475*, 242-248.
7. S.B. Ghorbel, F. Medina, A. Ghorbel and A.M. Segarra, *Appl. Catal. A-Gen.*, **2015**, *493*, 142-148.
8. M.G. Álvarez, A.M. Frey, J.H. Bitter, A.M. Segarra, K.P. de Jong and F. Medina, *Appl. Catal. B-Environ.*, **2013**, *134-135*, 231-237.
9. F. Rey, V. Fornes and J.M. Rojo, *J. Chem. Soc. Faraday T.*, **1992**, *88*, 2233.
10. E. Angelescu, O.D. Pavel, R. Bîrjega, M. Florea and R. Zăvoianu, *Appl. Catal. A-Gen.*, **2008**, *341*, 50-57.
11. E. Angelescu, O.D. Pavel, R. Zăvoianu and R. Bîrjega, *Rev. Roum. Chim.*, **2004**, *49*, 367-375.
12. O.D. Pavel, D. Tichit and I.-C. Marcu, *Appl. Clay Sci.*, **2012**, *61*, 52-58.
13. P.S. Kumbhar, J. Sanchez-Valente and F. Figueras, *Chem. Commun.*, **1998**, 1091-1092.

14. S.S. Chaphekar and S.D. Samant, *Appl. Clay Sci.*, **2003**, *242*, 11-15.
15. H. Kabashima, T. Katou and H. Hattori, *Appl. Clay Sci.*, **2001**, *241*, 121-124.
16. H. Hattori, *Appl. Clay Sci.*, **2001**, *222*, 247-259.
17. O.D. Pavel, R. Zăvoianu, R. Bîrjega and E. Angelescu, *Catal. Lett.*, **2011**, *12*, 845-850.
18. D. Debecker, E. M. Gaigneaux and G. Busca, *Chem-Eur. J.*, **2009**, *15*, 3920-3935.
19. K. Parida and J. Das, *J. Mol. Catal. A: Chem.*, **2000**, *151*, 185-192.
20. R. Ionescu, O.D. Pavel, R. Bîrjega, R. Zăvoianu and E. Angelescu, *Catal. Lett.*, **2010**, *134*, 309-317.
21. R. Bîrjega, O.D. Pavel, G. Costentin, M. Che and E. Angelescu, *Appl. Catal. A-Gen.*, **2005**, *288*, 185-193.
22. F. Teodorescu, M. Deaconu, E. Bartha, R. Zăvoianu, O. D. Pavel, *Catal. Lett.*, **2014**, *144*, 117-122.

