

Modifications of the Catalytic Activity for Cyanoethylation Induced by the Memory Effect of Mg/Al-Type Modified Hydrotalcites

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The aim of this work is to study the different changes of the structure, texture and surface morphology of Mg/Al hydrotalcite ($Mg_{0.75}Al_{0.23}$) modified by Y and La for a cationic chemical composition $Mg_{0.75}Al_{0.23}M^{III}_{0.02}$. The activity of these solids was tested in the cyanoethylation reaction of ethanol with acrylonitrile. The samples have been characterized by XRD, surface area and porous structure, TG-DTG and TEM.

Keywords: modified Mg/Al hydrotalcite, cyanoethylation reaction, base catalysts

The hydrotalcites (belonging to an anionic natural/synthetic mineral group [1, 2]) present a memory effect which is denoted as the reconstruction possibility of the "layered double hydroxides (LDH)" structure when the mixed oxides obtained by calcination of hydrotalcite parents up to 600°C are in contact with an aqueous solution containing different anions [2-4]. When the reconstruction of LDH structure takes place under reaction conditions, usually the "memory effect" is not desirable because the composition and structure of the solid suffers important modifications [5]. If the reconstruction is carried out in water, at room temperature, many OH⁻ anions are placed in the interlayer space leading to LDH-like solids which have active base sites for different catalytic reactions such as condensation, addition to the C-O bond, epoxidation, alkylation, acylation, etc [6-10]. Two mechanisms are proposed in the literature in order to explain the "memory effect". The first one is a retro-topotactic process involving Al³⁺ and Mg²⁺ cations located both in the octahedral sites of the mixed oxide [4]. The increase of the calcination temperature leads to the diffusion of the bivalent cations in the tetrahedral sites with formation of stable spinel structures. When the calcinations are carried out above 600°C all bivalent cations are placed in the tetrahedral sites and the memory effect disappears. The second one is a dissolution-recrystallization mechanism [11] involving the dissolution of some Mg²⁺ cations leading to their hydrolysis with formation of brucite-like structure in the presence of Al³⁺ due to the tendency of auto-organization which is the driving force in the formation of hydrotalcite by co-precipitation. The presence of ions in the solution makes possible their incorporation in the LDH structure by recrystallization. The recrystallization starts on the corners and defects of the mixed oxides structures and the hydrotalcite structures are reconstructed. However the reconstructed structures have different morphology compared to the parent structures.

This paper brings new insights concerning the reconstruction of the LDH-like phases in the case of Mg/Al hydrotalcites modified with trivalent lanthanide cations such as La³⁺ or Y³⁺. The modified hydrotalcite structures had the cationic chemical composition $Mg_{0.75}Al_{0.23}M^{III}_{0.02}$ ($M^{III} = La$, or Y). It has been assumed that the modification of the

hydrotalcite with trivalent lanthanide cations may lead to some particularities of the solids: such as different locations and dispersion of lanthanide cations in the rebuilt LDH, modification of surface areas, preferential incorporation of OH⁻ versus CO₃²⁻ in the interlayer space. Moreover these changes in the characteristics of the solids will be accompanied by differences in their catalytic activities and selectivities for the cyanoethylation of ethanol with acrylonitrile.

Experimental part

Catalysts Preparation

A classic hydrotalcite with formula $[Mg_{0.75}Al_{0.25}(OH)_2]^{0.25}A^n \cdot nH_2O$, where A is OH⁻ and CO₃²⁻ and atomic ratio $Me^{2+}/Me^{3+} = 3$, was prepared according to a procedure already described [12, 13]. The synthesis was carried out under low supersaturation conditions at pH=10 using a mixture of Na₂CO₃ and NaOH as adjusting pH solution. The chemical analysis had confirmed that the Mg/Al ratio is 3:1 as it was in the starting solution. The hydrotalcite sample named d-Mg/Al was calcined at 460°C in air atmosphere to obtain the corresponding mixed oxide denominated c-Mg/Al. The mixed oxide was then rehydrated by immersion in decarbonated water, and dried in air at 90°C for 24 h in order to reconstruct the LDH structure yielding the sample further called h-Mg/Al. The hydrotalcite obtained by hydration was then calcined at 460°C in air atmosphere to re-obtain the corresponding mixed oxide, yielding the sample rc-Mg/Al.

For the hydrotalcite samples modified with Y and La, the preparation method is similar to the method used for the unmodified samples Mg/Al. The only modification of the preparation method concerns the amount of the aluminium compound used in the synthesis of the dried hydrotalcite. In this case an amount corresponding to 2% moles of the aluminium compound used in the classical procedure were substituted by an equimolar amount of Y³⁺ or La³⁺ compounds in the co-precipitation step. The precursors for Y and La were hydrated nitrates. In order to easily identify the modified samples, they are referred analogously to the unmodified samples: d-Mg/Al+Y and d-Mg/Al+La respectively for dried samples, c-Mg/Al+Y and c-Mg/Al+La respectively for mixed oxides, h-Mg/Al+Y and

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h-Mg/Al+La respectively for rehydrated samples and rc-Mg/Al+Y and rc-Mg/Al+La respectively for re-calcined samples.

Characterization of catalysts

The X-ray powder diffraction patterns were collected on a DRON-3 X-ray diffractometer with a nickel filtered Cu K α radiation ($\lambda_{\text{Cu-K}\alpha} = 1.5418 \text{ \AA}$) in a 2θ range of 5–70°, a step width of 0.05° and an acquisition time of 2 s on each step.

The TG-DTG analysis was performed up to 500°C on a Setaram 92 equipment with a heating rate of 10°C/min.

The N₂ adsorption-desorption isotherms were obtained using Micromeritics-ASAP-2020 Instrument and the surface areas deduced using the BET equation.

The microstructural characterization (TEM) was carried out using a Philips-CM-10 electronic microscope.

Catalytic tests

Catalytic tests were performed in a glass batch reactor equipped with a condenser system. Acrylonitrile (0.01 mol) and ethanol (0.03 mol) were stirred and heated to the reflux temperature. Once the reaction temperature (90°C) was stabilized, the catalysts (3% weight) were added and the reaction started up. After 5 h reaction time the samples were 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 N₂ (99.999%) was used as carrier gas. Beta-ethoxypropionitrile was the prevailing reaction product.

Results and discussions

Catalysts characterization

The restoration of the original layered structure by the rehydration of the calcined modified and unmodified solids was confirmed by the XRD measurements (figs. 1 a-c).

The presence of the basal reflections (003) and (006) reflections upon rehydration confirms the reformation of the regular layered structure with a 3R symmetry for layer stacking, typical to LDHs. The patterns of the hydrated samples exhibit an increase of the overall crystallinity in all three cases.

The hydration of c-Mg/Al sample leads to a more ordered structure. The interlayer is probably populated especially with OH⁻ groups more than carbonate anions. The rc-Mg/Al sample obtained by calcination of h-Mg/Al corresponds to a mixed oxide with MgO-periclase structure.

The Y-modified samples show a similar behaviour as the reference rare-earth free samples. The h-Mg/Al+Y sample presents diffraction lines more intense compared to the d-Mg/Al+Y sample (fig. 1b). According to the structural data presented in table 1, the slight increase of the “c” parameter for d-Mg/Al+Y and h-Mg/Al+Y samples compared to d-Mg/Al and h-Mg/Al respectively stands for the partially intercalation of Y species into the interlayer. We have already reported this result for a series of REE species [12]. For the h-Mg/Al+Y sample a higher “c” parameter value, a decrease of the I_{003}/I_{110} ratio (table 1) and a higher disorder degree compared to the reference h-Mg/Al sample indicate the preservation of the presence of Y-species in the interlayer upon rehydration.

In the case of Mg/Al+La sample, low intensity diffraction lines corresponding to the La₂O₂CO₃ phase (La₂CO₅ – JCPDS 23-0320 and La₂(CO₃)₂(OH)₂ JCPDS 70-1774) can be observed (fig. 1c).

The electronegative character of La ($X_{\text{La}} = 1.1$) leads to formation of carbonate species. The ionic radius of La³⁺

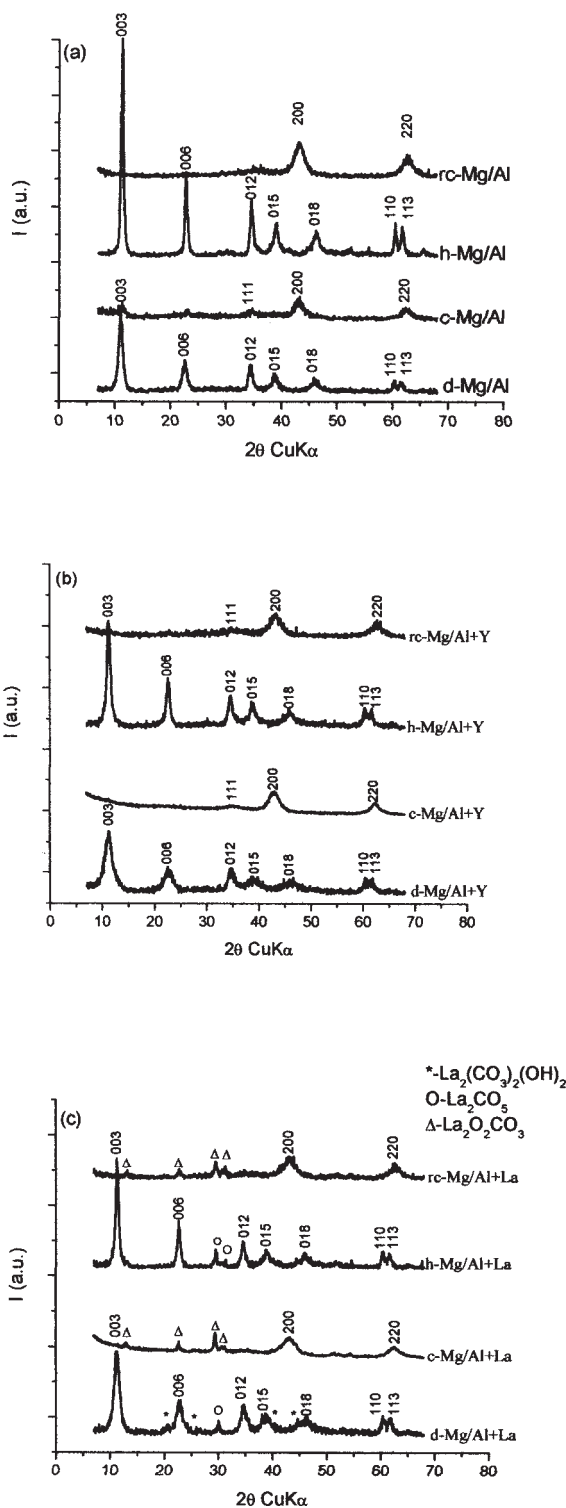


Fig. 1. Powder X-ray diffraction of the unmodified samples (a); Y - modified samples (b); La- modified samples (c)

(1.032 Å) is too large to allow the intercalation of La³⁺ ions into the interlayer space. In the case of c-Mg/Al+La sample, an isolated phase La₂O₂CO₃ (JCPDS 48-1113) is detected probably due to re-adsorption of CO₂ generated by decomposition of hydrotalcite under thermal treatment or to a contamination by CO₂ from air. The formation of this phase is due to the stronger base character of lanthanum and to the higher reactivity of the lanthanum species located outside the hydrotalcite crystallites. After hydration, La₂(CO₃)₂(OH)₂ is not formed; lanthanum ions are present as oxycarbonate species. The lanthanum species are likely to be deposited on the external surface of the LDH crystals and do not cancel the memory effect of the hydrotalcite.

Table 1
THE STRUCTURAL PARAMETERS OF LDH SAMPLES

Samples	Structural data						
	a (Å)	c (Å)	IFS (Å)*	Δ (%)**	I ₀₀₃ /I ₁₁₀	I _{h003} /I _{d003}	I _{h110} /I _{d110}
d-Mg/Al	3,069	23,643	3,08	2,48	7,35	3,01	2,57
h-Mg/Al	3,061	23,347	2,98	0,97	8,43		
d-Mg/Al+Y	3,070	23,880	3,16	3,48	5,08	1,84	1,75
h-Mg/Al+Y	3,068	23,637	3,08	2,00	6,98		
d-Mg/Al+La	3,070	23,680	3,09	3,12	4,67	1,238	0,820
h-Mg/Al+La	3,065	23,483	3,03	2,34	8,07		

* IFS=c/3-4.8Å, where 4.8 Å is the thickness of the brucite-like layer [14].

** Δ (%) is calculated as the ratio between the FWHM (full width at half maximum) and the area of the (0 0 3) peak.

The data presented in table 1 show also the increase of the ratio I_{003}/I_{110} for the hydrated samples compared to the dried samples suggesting a modification of the interlayer anionic composition. The parameter IFS decreases because the number of OH⁻ groups after hydration is higher than CO₃²⁻. The decrease of disorder degree along *c*-axis is due to the ordered arrangement of anionic species. Such effects are correlated with the increase of the diffraction intensity observed for hydrated form compared to the dried form (I_{h003}/I_{d003} respectively I_{h110}/I_{d110}). The crystallinity is higher for Mg/Al compared to that of the Y- and La- modified samples leading to the conclusion that the presence of species with great molecular size in the interlayer or on the surface makes the structure less flexible, hindering the diffusion of small sized anionic species in the interlayer. Table 2 presents the structural and textural data for the mixed oxides.

For the recalcined samples there are some modifications: the "a" parameters, the Δ(%) and surface area decrease; the crystallinity increases (I_{rc200}/I_{c200}). The effect is more pronounced for the unmodified sample.

Figure 2 presents the TG-DTG diagrams for d-Mg/Al and h-Mg/Al samples.

The first maximum weight loss at 205.63°C and 203.8°C respectively is assigned to the loss of water and a small amount of CO₂ (d-Mg/Al 14.368% H₂O, 0.423% CO₂; h-Mg/Al 14.575% H₂O, 0.084% CO₂).

The water amount for the second domain which is assigned to OH⁻ bonded to the Al³⁺ cations for the h-Mg/Al sample (5.235%) are lower compared to that found for the

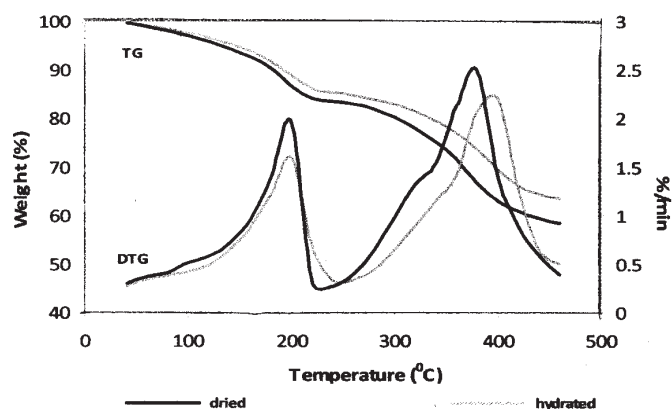


Fig. 2. DTG-TG diagrams for d-Mg/Al and h-Mg/Al samples

d-Mg/Al sample (5.740%). This lower amount of water loss observed for the h-Mg/Al sample is due to the formation of stable spinels in the calcined hydroxaltes which are not further able to recover the LDH structure by hydration. The amount of CO₂ for d-Mg/Al sample is 0.459% and for h-Mg/Al sample is 0.061%. The third domain of weight loss corresponds to the removing of OH⁻ from brucite structure and of the remaining CO₂ from interlayer carbonate anions. The quantity lost is higher for h-Mg/Al sample (18.990%) than for d-Mg/Al sample (15.060%) which is in agreement with our supposition that carbonate anions are removed upon calcination and the amount of OH⁻ is higher after rehydration. The maximum temperature of the third domain is a little bit higher for h-Mg/Al sample than for d-

Table 2
THE STRUCTURAL AND TEXTURAL PARAMETERS OF MIXED OXIDES

Samples	Structural data			Textural data
	a (Å)	Δ (%)*	I _{rc200} /I _{c200}	Surface area (m ² /g)
c-Mg/Al	4,199	1,08	1,85	188
rc-Mg/Al	4,179	0,65		157
c-Mg/Al+Y	4,210	1,28	1,07	221
rc-Mg/Al+Y	4,182	1,27		164
c-Mg/Al+La	4,193	1,79		140
rc-Mg/Al+La	4,192	1,23		130

** Δ (%) is calculated as the ratio between the FWHM (full width at half maximum) and the area of the (200) peak.

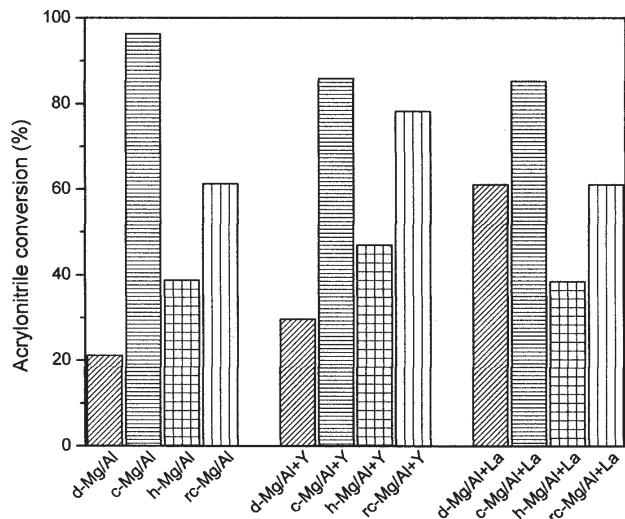


Fig. 3. The TEM pictures of d-Mg/Al, c-Mg/Al and h-Mg/Al respectively

Mg/Al sample (404.05°C; 393.13°C respectively). The CO_2 removed corresponds to 0.560% and 1.710% for h-Mg/Al and d-Mg/Al samples, respectively. For the modified samples the modifications are not very important.

Figure 3 presents the TEM pictures of d-Mg/Al, c-Mg/Al and h-Mg/Al respectively.

The d-Mg/Al TEM picture shows the regular hexagonal shape characteristic to the LDH structure (a). The c-Mg/Al preserves the hexagonal shape of hydrotalcite (b). The crystallites size of these mixed oxides is smaller because water and CO_2 are removed from interlayer and from hydrotalcite structure after calcination. Taking into account the hexagonal structure, the hydrotalcite possess the memory effect since c-Mg/Al is an unstable spinel. After hydration, the LDH structure is rebuilt with some irregularities. The texture of h-Mg/Al sample is different than d-Mg/Al sample because the surface area decreases and the main pore size increases. For the samples modified with Y and La the TEM images are similar to those of the unmodified samples.

Results of catalytic tests

The modification of catalytic activity observed for the Mg/Al samples which present memory effect in the cyanoethylation reaction of ethanol with acrylonitrile can be explained taken into account the structural and textural characteristics of this sample. In all cases, the selectivity to the main product (beta-ethoxypropionitrile) was higher than 98%. From the results presented in figure 4 it may be seen that d-Mg/Al is less active than c-Mg/Al.

By hydration of c-Mg/Al, the LDH structure is rebuilt and the catalytic activity of the reconstructed sample h-Mg/Al is double compared to d-Mg/Al. This increase of activity can be attributed to 3 factors: a) partial replacing of CO_3^{2-} with more basic OH^- anions and the smaller size of h-Mg/Al crystallites compared to those of d-Mg/Al catalyst; b) the different basicity of the solids and the different distribution of base sites in these two samples; c) the defects on the surface of the catalysts and the different crystallinity degrees of d-Mg/Al and h-Mg/Al respectively. The recalcination of h-Mg/Al sample leads to the mixed oxides with lower activity than c-Mg/Al. This fact is due to the decrease of the surface area of rc-Mg/Al sample and to an eventual increase of the crystallite size. For d-Mg/Al+La sample the activity is due to $\text{La}_2\text{O}_2\text{CO}_3$ phases and $\text{La}_2(\text{CO}_3)_2(\text{OH})_2$ which are on the surface of hydrotalcite crystallites. This activity may be due even to a synergism

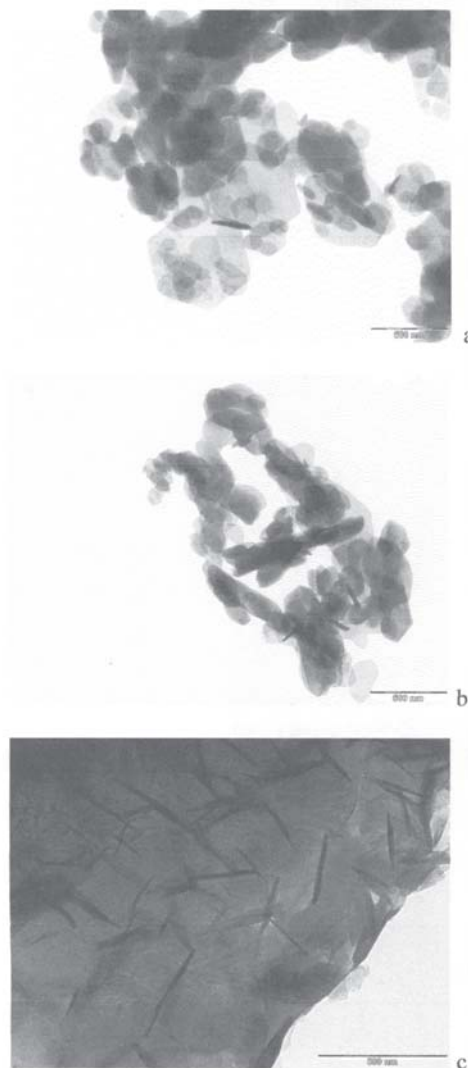


Fig. 4. The activity of unmodified and modified catalysts after 5 hours reaction time

between hydroxylated lanthanum species, more basic than $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$. For h-Mg/Al+La sample the activity is the same as the one for h-Mg/Al because after calcination La^{3+} which cannot enter in the interlayer of the hydrotalcite-type structure is converted to $\text{La}_2\text{O}_2\text{CO}_3$ which is preserved even in the recalcined sample; therefore, the memory effect is corresponding only to d-Mg/Al hydrotalcite.

For the samples modified with Y the trend of activity is similar to that noticed on the unmodified samples, however the levels of the conversion are higher due to the stronger base character of Y. For both groups of modified samples the decreases of activity for the recalcined forms are due to the decreases of surface area and the increases of crystallite sizes.

Conclusions

The experiments on the memory effect of Y and La modified hydrotalcites show that the LDH structure is recovered by the hydration treatment applied on their derived mixed oxides. The OH^- number increases at the expense of CO_3^{2-} in the hydrated samples leading to an increase of their catalytic activity for the cyanoethylation of ethanol with acrylonitrile. The effects are less evident for h-Mg/Al+La sample due to the absence in the hydrated form of the more active $\text{La}_2(\text{CO}_3)_2(\text{OH})_2$ species which were detected in the dried form. For h-Mg/Al+Y sample the cumulative effect of the replacement of weak base carbonate sites by stronger base OH^- sites and the presence

of interlayer Y species is to be considered responsible for the increase of the activity upon rehydration. The modifications of original hydrotalcite structures with Y and La and the exploitation of the “memory effect” lead to new materials with different activity in the cyanoethylation reaction.

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References

1. POPOVICI E., PODE R., REISZ E., COCHECI L., PODE V., SEFTEL, E. M. Rev. Chim. (Bucharest), **58**, no. 1, 2007, p. 13
2. CAVANI, F., TRIFIRO, F., VACCARI, A., Catalysis Today, **11**, 1991, p. 173
3. REY, F., FORNES, V., ROJO, J. M., Journal of the Chemical Society, Faraday Transactions, **88**, no.15, 1992, p. 2233
4. ANGELESCU, E., PAVEL, O.D., BÎRJEGA, R., FLOREA, M., ZĂVOIANU, R., Applied Catalysis A: General, **341**, 2008, p. 50
5. MARCHI, A. J., APESTEGUIA, C. R., Applied Clay Science, **13**, 1998, p. 35
6. ANGELESCU, E., PAVEL, O.D., BÎRJEGA, R., ZĂVOIANU, R., COSTENTIN, G., CHE, M., Applied Catalysis A: General, **308**, 2006, p. 13
7. SELS, B. F. De VOS, D. E., JACOBS, P. A., Catal. Reviews, **43**, 2001, p. 443
8. PALOMEQUE, J., LOPEZ, J., FIGUERAS, F., Journal of Catalysis, **211**, 2002, p. 150
9. VELU, S., SWAMY, C. S., Applied Catalysis A: General **119**, 1994, p. 241
10. WATANABE, Y., TATSUMI, T., Microporous and Mesoporous Materials, **22**, 1998, p. 399
11. TAKEHIRA, K., KAWABATA, T., SHISHIDO, T., MURAKAMI, K., OHI, T., SHORO, D., HONDA, M., TAKAKI, K., Journal of Catalysis, **231**, 2005, p. 92
12. BÎRJEGA, R., PAVEL, O. D., COSTENTIN, G., CHE, M., ANGELESCU, E., Applied Catalysis A: General, **288**, 2005, p. 185
13. PAVEL, O. D., BÎRJEGA, R., CHE, M., COSTENTIN, G., ANGELESCU, E., ȘERBAN, S., Catalysis Communications, **9**, 2008, p. 1974
14. MIYATA, S., Clays Clay Mineral, **23**, 1975, p. 369

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