Catalysis Today 139 (2008) 161–167

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrotalcite docked Rh-TPPTS complexes as efficient catalysts for the arylation of 2-cyclohexen-1-one in neat water

F. Neaţu [a,1], M. Besnea [a,1], V.G. Komvokis [b], J.-P. Genêt [c], V. Michelet [c,*], K.S. Triantafyllidis [d,*], V.I. Pârvulescu [a,1,*]

[a] University of Bucharest, Department of Chemical Technology and Catalysis, B-dul Regina Elisabeta 4-12, Bucharest 030016, Romania
[b] Chemical Process Engineering Research Institute, CERTH, 57001 Thessaloniki, Greece
[c] Laboratoire de Synthèse Sélective Organique et Produits Naturels, ENSCP, UMR 7573, 11 rue P. et M. Curie, F-75231 Paris Cedex 05, France
[d] Aristotle University of Thessaloniki, Department of Chemistry, University Campus, P.O. Box 116, 54124, Thessaloniki, Greece

ARTICLE INFO

Article history:
Available online 11 September 2008

Keywords:
Hydrotalcites
Rhodium
TPPTS
Heterogeneization
Arylation
Boronic acids
1,4-addition

ABSTRACT

Well defined layered-double hydroxides (LDH: $Mg_3Al–NO_3/CO_3$, $Mg_3Ga–NO_3/CO_3$, $Zn_2Al–NO_3/CO_3$ and $Zn_2Ga–NO_3/CO_3$) were prepared using typical procedures starting from $Mg(NO_3)_2·6H_2O$, $Zn(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$ and $Ga(NO_3)_3·H_2O$. Rh-TPPTS complex was prepared by simple complexation of a Rh precursor $[Rh(cod)Cl]_2$ and TPPTS (3,3′,3″-phosphanetriyl benzenesulfonic acid) in water. The heterogeneization of the Rh-TPPTS complex was performed by anionic exchange between Rh-complex and LDH supports. The catalysts' structures and the chemical composition were confirmed by chemical analysis, XRD patterns, XP, FTIR and DRIFT spectroscopy. LDH-substituted Rh-TPPTS heterogeneous catalysts showed good catalytic activity in the 1,4-addition of arylboronic acid to 2-cyclohexen-1-one.

1. Introduction

Over the past few years, significant research has been directed in the application of water as solvent in organic syntheses and in homogeneous transition metal catalyzed reactions. Indeed, water is not toxic and inflammable, and as an attractive feature it is expected to be intensively used in the development of efficient, environmentally safe systems [1,2].

In 1997, Miyaura and co-workers reported a Rh-catalyzed 1,4-addition of organoboron reagents to α,β-unsaturated carbonyl compounds [3a]. After that, substantial research activity was engaged in the area of Rh-catalyzed homogeneous carbon–carbon bond formations [4–8]. Although these homogeneous catalytic systems led to excellent results, their use suffers from disadvantages such as requirements for toxic and expensive phosphane and tedious work-up procedures [5,6,8]. Heterogeneous catalysts can provide an alternative to these systems and the utilization of layered clays, exhibiting strong acid or base active sites, offers very promising examples [9,10]. Hydrotalcites are layered mixed hydroxides (LDH – layered double hydroxides) of two metallic species M^{2+} and M^{3+} [11–13]. Moreover, they may provide a tunable basicity of the surface. They already play a crucial role in designing promising solid base catalysts [10–12,14]. Due to their specific structure they exhibit anionic exchange properties, and by changing the nature of M, both the surface basicity and the adsorption capacity can be tailored [13–15]. The association of an LDH with an active metal leads to bifunctional catalysts in which not only the activity, but also the selectivity is dramatically enhanced [16]. The insertion of metallic species by replacing the inter-layer coordination sphere is the principle used to generate a large family of catalysts with multiple applications [17,18]. A $RhCl_3·nH_2O$ ionic-exchanged LDH heterogeneous system was recently reported [19]. However, it is not clear from the provided description which anion of $RhCl_3·nH_2O$ has been exchanged with the LDH anions. The addition of arylboronic acid to cyclohexenones required the supplementary addition of 1,5-cyclooctadiene (1,5-cod) and 1,4-dioxane as solvent. No activity was observed in water.

In this paper we describe the synthesis of four hydrotalcite-like materials containing as building block the elements Mg, Zn, Al and Ga followed by the immobilization of the Rh(I)$(TPPTS)_3$Cl water-soluble complex in the above LDH in water. The characterization of

---

[*] Corresponding author.
E-mail addresses: veronique-michelet@enscp.fr (V. Michelet), ktrianta@chem.auth.gr (K.S. Triantafyllidis), v_parvulescu@chem.unibuc.ro (V.I. Pârvulescu).
[1] Tel.: +40 214100241; fax: +40 214100241.

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.07.028

the resulted catalysts using ICP-AES, powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), FTIR and DRIFTs, and their catalytic behavior for the 1,4-addition of arylboronic acid to 2-cyclohexen-1-one in water are reported.

2. Experimental

2.1. Catalysts preparation

2.1.1. Synthesis of the layered double hydroxides (LDH)

The Mg_3Al-LDH was synthesized based on a well-established procedure [20]. In a typical synthesis, an aqueous solution containing 0.3 mol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.1 mol of $Al(NO_3)_3{\cdot}9H_2O$ was slowly added to an aqueous solution containing 0.25 mol $Na_2CO_3{\cdot}10H_2O$ under vigorous stirring at room temperature, maintaining the pH between 8 and 10 by adding dropwise a 50% (w/w) NaOH aqueous solution. After initial mixing of all the solutions the solid–liquid dispersion was stirred for 2 h at room temperature and then for 18 h in sealed polypropylene bottles at 65 °C (±2 °C). The precipitate was filtered, washed with bidistilled water (nitrates free) and were dried at room temperature overnight. The produced sample was denoted Mg_3Al-LDH.

The Ga-substituted LDH (Mg_3Ga-LDH) was synthesized following the above procedure, except that 0.1 mol of $Ga(NO_3)_3{\cdot}H_2O$ aqueous solution was used instead of the aluminum nitrate solution and the pH during mixing of the solutions and aging of the suspension was kept at the value of ~10.

The Zn-substituted LDH (Zn_2Al-LDH and Zn_2Ga-LDH) were synthesized as the Ga-substituted one with the use of 0.2 mol of $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solution instead of magnesium nitrate solution and 0.1 mol of $Al(NO_3)_3{\cdot}9H_2O$ or $Ga(NO_3)_3{\cdot}H_2O$ aqueous solutions, respectively.

2.1.2. Synthesis of the catalysts (Rh-TPPTS immobilized on LDH)

The synthesis of the Rh-ligand complex was carried out under inert atmosphere (argon) to avoid any oxidation of the TPPTS ligand. All the steps used degassed water. The degasification of water was carried out repeating five times the following procedure: first, evacuation of water under vacuum and a vigorous stirring, second purging argon through it. To a 2.5×10^{-3} M degassed aqueous solution of $[Rh(cod)Cl]_2$ (50 mL), was added 1 mmol of TPPTS keeping the system under vigorous stirring for 12 h. The preparation of Rh-TPPTS/LDH catalysts was carried out using the ion exchange method under the same inert atmosphere. To the above mixture 1 g of LDH was added. Based on the M^{3+} content (wt.% determined by ICP-AES chemical analysis) of the parent LDH samples, the mole ratio in the synthesis mixture of the $-SO_3^-$ groups (three per TPPTS ligand) to the exchangeable anions of the parent LDHs was: 2.7 for Mg_3Al-LDH, 3.3 for Mg_3Ga-LDH, 3.0 for Zn_2Al-LDH, and 4.8 for Zn_2Ga-LDH. The stirring was continued for another 24 h in order to allow exchange between the anions to reach equilibrium. Then, the solid obtained was separated by centrifugation, washed thoroughly with bidistilled degassed water and dried under vacuum at 60 °C for 16 h. The obtained samples were denoted as Rh-TPPTS/Mg_3Al-LDH, Rh-TPPTS/Mg_3Gal-LDH, Rh-TPPTS/Zn_2Al-LDH and Rh-TPPTS/Zn_2Ga-LDH, respectively.

2.2. Catalysts characterization

Chemical composition of the catalysts was determined by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) using a Plasma 40, PerkinElmer equipment after appropriate dissolution of the solid samples. Both LDH supports and exchanged catalysts were characterized by powder X-ray diffraction (XRD) using a Siemens D-5000 automated diffractometer (Cu-Kα radiation, λ = 1.5418 Å) operating at 45 kV and 100 mÅ; counts were accumulated in the range of 5–85° 2θ every 0.02° and with a counting time of 2 s per step. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Leybold Heraeus spectrometer with monochromated Al-Kα radiation. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ peak (binding energy: 84.0 eV). For the calculation of the binding energies, the C 1s peak of the C–(C,H) component at 284.8 eV was used as an internal standard. The superficial composition of the investigated samples was determined using the apparatus software. The binding energies assigned to the $Rh3d_5$, $Al2p_3$, $Zn2p_3$, $Mg2p_3$, $Ga3d_5$, O1s, C1s, $P2p_3$, and $S2p_3$ levels were analyzed. FTIR experiments were conducted on a Brucker IFS88 using the KBr technique for preparing the pellets and the following parameters: 200 scans, 500–4000 cm^{-1} scan range, 4 cm^{-1} resolution. DRIFTs investigation of the catalysts was realized with a Nicolet 4700 spectrometer using the following parameters: 200 scans, 600–4000 cm^{-1} scan range, 4 cm^{-1} resolution.

2.3. Catalytic tests

The heterogeneous Rh-TPPTS/LDH catalyst was added to a mixture of arylboronic acid (1.15 mmol), Na_2CO_3 (0.92 mmol), 2-cyclohexen-1-one (0.46 mmol) and water (2.2 mL). The above mixture was heated at 80 °C until completion of the reaction (TLC) and then cooled to room temperature. The reaction mixture was filtered on a short pad of silica gel with cyclohexane:ethyl acetate (7:3) and evaporated under reduced pressure. No further purification was necessary. The purity of the product (>98%) was checked by ^1H and ^{13}C NMR and GC-MS analyses.

3. Results and discussions

3.1. Catalysts characterization

3.1.1. Characterization of the layered double hydroxides (LDH)

The XRD patterns of all the synthesized samples (Mg_3Al, Mg_3Ga, Zn_2Al and Zn_2Ga-LDH) shown in Fig. 1, exhibit the characteristic reflections of the hydrotalcite structure and accordingly, the pattern can be indexed in a hexagonal lattice with an R3m rhombohedral space group symmetry. The high intensity of the main reflections, i.e. the (0 0 3) at ~11–12° 2θ, the (0 0 6) at ~23° 2θ, and the (0 1 2) at ~34–35° 2θ, reveals that the samples are highly crystalline. Only in the case of Zn_2Ga-LDH the formation of a

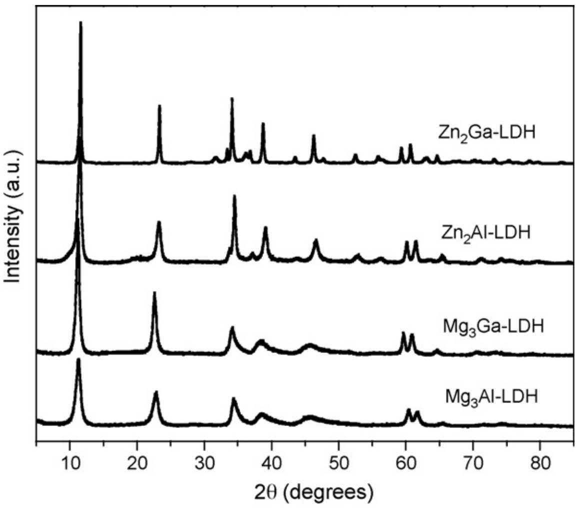


Fig. 1. XRD patterns of synthesized LDHs.

Table 1
Composition and structure characteristics of LDH samples

Samples	Composition (M^{2+}/M^{3+} mole ratio)[a]	Lattice parameters			
		$d_{(0\,0\,3)}$ (Å)	$d_{(1\,1\,0)}$ (Å)	a (Å)	c (Å)
Mg_3Al-LDH	2.39 (3)[b]	7.838	1.531	3.062	23.514
Mg_3Ga-LDH	2.93 (3)	7.891	1.549	3.098	23.673
Zn_2Al-LDH	1.84 (2)	7.715	1.537	3.074	23.145
Zn_2Ga-LDH	2.84 (2)	7.621	1.556	3.112	22.863

[a] From ICP-AES chemical analysis.

[b] Number in parentheses refer to mole ratio in the synthesis mixture.

crystalline ZnO phase was identified, whose reflections however have very low intensity compared to those of the Zn-Ga layered double hydroxide structure. The parameter a which corresponds to the cation–cation distance in the brucite-like layer of the LDH samples has been calculated from the d-spacing of the (1 1 0) reflection ($a = 2 \times d_{1\,1\,0}$). The parameter c which is related to the thickness of the brucite-like layers and the interlayer space, has also been calculated from the d-spacing of the (0 0 3) reflection ($c = 3 \times d_{0\,0\,3}$). The respective data are given in Table 1. The values of the crystallographic parameters a and c (3.062 and 23.514 Å, respectively) are slightly higher (mainly of c parameter) than those expected for a Mg–Al hydrotalcite sample with Mg/Al ~3 and CO_3^{2-} as charge-balancing anions, because of the presence of nitrates in the interlayer space which increase the value of c parameter [13a,21]. The isomorphous substitution of Al^{3+} (with ionic radius 0.50 Å) for Ga^{3+} (ionic radius 0.62 Å) in the LDH structure (sample Mg_3Ga-LDH) resulted in slightly higher α value (3.098), as was also shown previously [22]. Although Mg^{2+} (ionic radius 0.65 Å) was substituted by the larger Zn^{2+} (ionic radius 0.74 Å) in sample Zn_2Al-LDH, the decrease of the M^{2+}/Al^{3+} ratio (from 3 to 2) resulted in a smaller increase of the α value (3.074) in this sample (compared to that for Mg_3Ga-LDH). Further substitution of Al^{3+} for Ga^{3+} (sample Zn_2Ga-LDH) induced further increase of the α value (3.112). It is noteworthy that the increase in the α value induced by substitution of Al^{3+} for Ga^{3+} in both the Mg and Zn-LDH samples is similar. The reported values of the crystallographic parameters a and c for the ZnAl- and ZnGa-containing LDH samples are similar to those previously reported [23,24].

The chemical analysis by ICP-AES showed that the determined M^{2+}/M^{3+} ratio in all the synthesized samples (Table 1), except for sample Zn_2Ga-LDH, was similar to the nominal ratio used in the synthesis mixture, indicating the successful formation of the LDH structure in accordance with the XRD results. The Zn/Ga ratio for the sample Zn_2Ga-LDH was slightly higher than 2 due to the presence of a small ZnO phase, also evidenced by XRD.

The FTIR spectra shown in Fig. 2 are typical of these type of layered materials. The relatively broad band at ~3500 cm^{-1} is attributed to O–H stretching vibration of hydrogen-bonded hydroxyl groups and of water molecules, which also has a bending vibration mode corresponding to the band recorded at ~1625 cm^{-1}. The bands at ~1360 cm^{-1} and 1450 cm^{-1} are attributed to nitrates and carbonates, respectively [21,25]. It is clearly evident that there is a significant portion of nitrates in the interlayer space of all the parent LDH samples, despite the high affinity of the LDH hydrotalcite structure for carbonates when these are present in the synthesis mixture either as precipitation reagent or as "impurities" from air (both cases apply in the present study). The concentration of NO_3^- varies in the order $Mg_3Al > Z\text{-}Zn_2Al > Mg_2Ga > Zn_2Ga$.

3.1.2. Characterization of the catalysts (Rh-TPPTS/LDH)

XRD analysis gave evidence of the partial ionic exchange of the prepared LDHs with the Rh-TPPTS complex (Fig. 3). The resulted catalysts contain two phases with distinct, well-ordered layered structure, one containing only the NO_3^-/CO_3^{2-} anions (initial phase/structure, with the same $d_{0\,0\,3}$ basal spacing) and another containing the docked Rh-TPPTS complex and the NO_3^-/CO_3^{2-} anions (higher $d_{0\,0\,3}$ basal spacing with the respective reflection shifted to lower 2θ values). The four harmonics, i.e., at 2θ 5° (0 0 3), 11° (0 0 6), 17° (0 0 9) and 23° (0 0 1 2) attributed to the latter phase that contain both the initial NO_3^-/CO_3^{2-} anions and the Rh-TPPTS complex, can be seen in the magnification of the 5–30 2θ range in Fig. 3. The (0 0 6) and (0 0 1 2) reflections are overlapped by the (0 0 3) and the (0 0 6) reflections of the NO_3^-/CO_3^{2-} phase of the parent LDH samples. The intensity of the peaks assigned to the mixed phase containing the Rh-TPPTS complex is low indicating the relatively small contribution of this phase and the low extent of ion-exchange of Rh-complex for the inorganic anions. Nevertheless, the observed shift of the (0 0 3) reflection to lower 2θ values corresponds to an increase of the $d_{0\,0\,3}$ basal spacing from ~7.7 Å for the parent LDH to ~15.2 Å for the Rh-TPPTS docked LDH samples. The $d_{0\,0\,3}$ basal spacing value of ~15.2 Å corresponds to the interlayer space (gallery) plus the thickness of one layer of the LDH structure. If we consider that the thickness of one layer of the brucite structure is 4.8 Å then the gallery height left is about 10–11 Å. This space is enough to accommodate only one molecule of ligand (TPPTS) and not the whole Rh-TPPTS complex. A partial penetration of the ligand inside the gallery can be visualized at the edges of some tactoids (small groups) of LDH layers, as it can be seen in Fig. 4. This structure, if optimized via increasing the Rh-complex loading at the edges of the tactoids, it could be preferred over the complete loading of the whole gallery with Rh-complex since the Rh atoms in the former case would be more easily accessible by the relatively large organic reactant molecules. In that case, all of the docked Rh metal/complex is expected to be utilized.

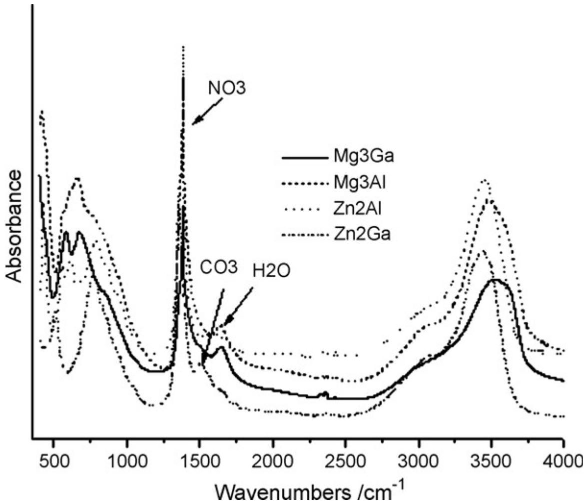


Fig. 2. FTIR spectra of Mg_3Ga-LDH, Mg_3Al-LDH, Zn_2Ga-LDH, and Zn_2Al-LDH.

The FTIR spectra of the exchanged samples (spectra not shown) indicate a decrease of the intensity of the band assigned to NO_3^- species. The percentage of the band due to CO_3^{2-} remained unchanged. According to these spectra the ionic exchange took place between the NO_3^- and the Rh-ligand complex, and not between the CO_3^{2-} and Rh-ligand complex as it was expected due to the high affinity of hydrotalcite structure for the CO_3^{2-} anions.

DRIFT analysis completed the structural information about these catalysts. The comparison of the DRIFT spectra of, e.g. Zn_2Ga-LDH and Rh-TPPTS/Zn_2Ga-LDH, reveals that the layered structure of the LDH is preserved after the ionic exchange and that the Rh-

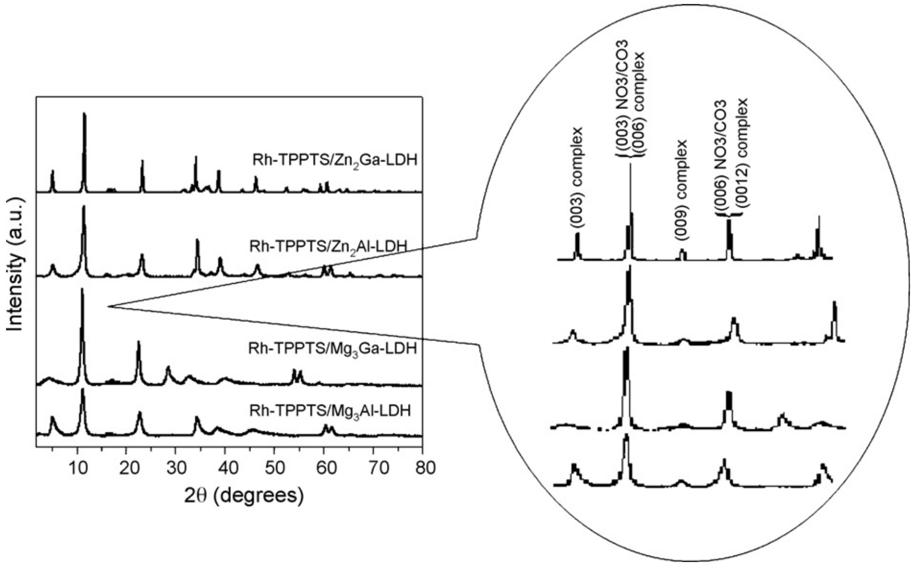


Fig. 3. XRD patterns of LDHs with the docked Rh/TPPTS complex. The magnification of the 2θ range from 5 to 30° shows the four harmonics for the mixed phase containing the Rh-TPPTS complex and the NO_3^-/CO_3^{2-} anions, and the two harmonics corresponding to the initial phase containing only the inorganic anions.

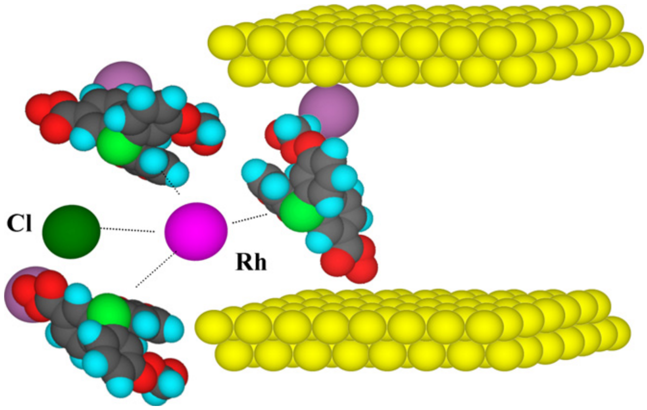


Fig. 4. Visualization of the docked Rh(I)$(TPPTS)_3Cl$ complex at the edges of LDH layers tactoids via insertion of one ligand in the gallery area.

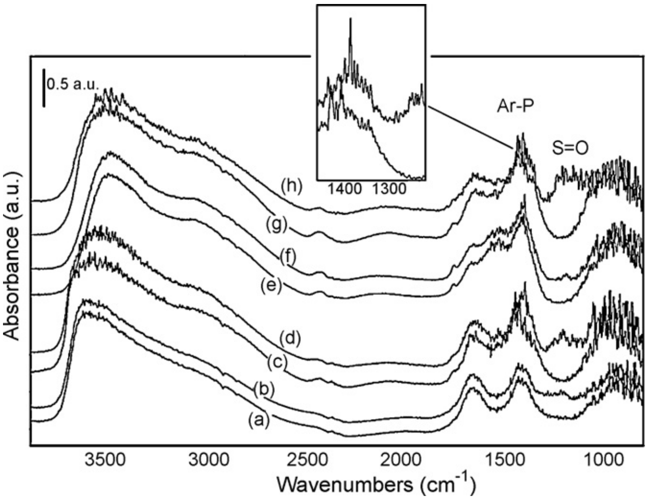


Fig. 5. DRIFT spectra of (a) Mg_3Ga-LDH, (b) Rh-TPPTS/Mg_3Ga-LDH, (c) Mg_3Al-LDH, (d) Rh-TPPTS/Mg_3Al-LDH, (e) Zn_2Ga-LDH, (f) Rh-TPPTS/Zn_2Ga-LDH, (g) Zn_2Al-LDH and (h) Rh-TPPTS/Zn_2Al-LDH.

TPPTS complex also preserves unaltered its structure (Fig. 5). As it can be seen from Fig. 5, the Rh-TPPTS complex is present in all the ionic exchanged hydrotalcites. Typical bands for TPPTS (1260–1210 cm^{-1} for S═O and ~1400 cm^{-1} for Ar-P vibrations) can be observed in these spectra.

XPS composition was in a very good agreement with chemical analysis results. As it can be seen in Table 2, the binding energies of the constitutive elements in LDHs are typical for their oxidation states, while for Rh it corresponds to (I) state [26] that is again in accordance with the oxidation state of the expected complex. ICP-AES analysis of the Rh exchanged LDH indicated a similar Rh content in all four samples. The TPPTS:Rh (wt.%) ratio was found to be a value of 2.83, in agreement with the structure of the expected complex [17c].

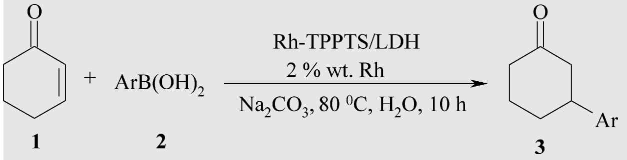
3.2. Catalytic results

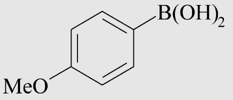
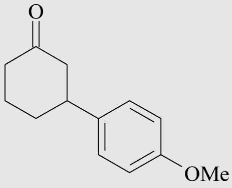
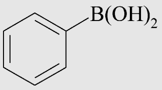
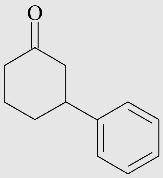
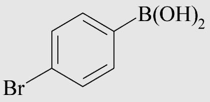
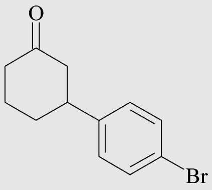
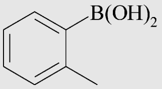
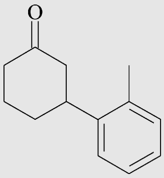
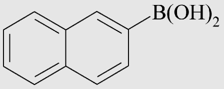
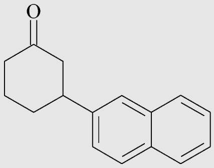
As mentioned above, the 1,4-addition of various arylboronic acids (**2**, Table 3) to 2-cyclohexen-1-one (**1**) was chosen as a standard reaction to evaluate the activity of the Rh-TPPTS/LDH

Table 2
XPS binding energies and atomic Rh:Zn XPS ratios

Catalyst	XPS binding energies (eV)						XPS composition	
	Al2p	Mg2p3	Zn2p3	Ga3d$_5$	P2p	Rh3d$_5$	Rh:Zn ratio	Rh:Mg ratio
Rh-TPPTS/Mg_3Al-LDH	74.1	51.1	–	–	132.7	308.2	–	0.092
Rh-TPPTS/Mg_3Ga-LDH	–	51.4	–	20.7	132.5	308.1	–	0.105
Rh-TPPTS/Zn_2Al-LDH	73.9		1021.6	–	132.6	308.2	0.059	–
Rh-TPPTS/Zn_2Ga-LDH	–		1021.9	20.8	132.6	308.2	0.041	–

Table 3
1,4-Addition of arylboronic acid (**2**) to 2-cyclohexen-1-one (**1**) over Rh-TPPTS/Mg_3Al-LDH catalyst



Entry	Boronic acid	Product	Yield[a] (%)
1	 **2a**	 **3a**	98
2	 **2b**	 **3b**	98
3	 **2c**	 **3c**	90
4	 **2d**	 **3d**	85
5	 **2e**	 **3e**	20

[a] Isolated yield based on **1**.

catalysts. 3,3′,3″-Phosphanetriyl benzenesulfonic acid (TPPTS) [27] was employed as ligand enabling both the solubilization in water of the Rh complex and the ionic exchange of the formed complex with the anions of the hydrotalcites. LDH was expected to be not a simply spectator acting as a host of the active Rh complex, but also to improve the activity of the Rh complex, as a result of its basicity.

Table 3 compiles the results using Rh-TPPTS/Mg_3Al-LDH catalysts in 1,4-addition of **2** to **1**. The use of the above catalyst led very efficiently to the arylated cyclohexenones, with up to 98% isolated yield (entries 1–4). The addition of either 4-methoxyphenyl or phenylboronic acid afforded the ketones **3a** and **3b** in 98% yield (entries 1, 2). The reaction conditions were compatible with a bromo atom as the substituted ketone **3c** was isolated in 90% yield (entry 3). The *ortho*-tolylboronic acid was introduced in 85% yield (entry 4). The introduction of a bulkier boronic acid such as 2-naphtylboronic acid was surprisingly more difficult (entry 5), which may be due to the difficulty of a bulky reactant to reach the catalytic active sites.

Replacing Rh-TPPTS/Mg_3Al-LDH catalyst with Rh-TPPTS/Zn_2Al-, Mg_3Ga-, or Zn_2Ga -LDH catalysts resulted in lower yields (Table 4). The higher reactivity of 4-methoxyboronic acid and phenylboronic acid was a general trend for all the catalysts. In the same manner as with the Rh-TPPTS/Mg_3Al-LDH catalyst (Table 3), lower yields (15-60%) were obtained in the case of 4-bromo or 2-methylboronic acids. No reaction was observed in the case of the naphtylboronic acid.

Comparing the results given in Tables 3 and 4, it becomes evident that the activity of the catalysts decreases in the following sequence: Rh-TPPTS/Mg_3Al-LDH > Rh-TPPTS/Zn_2Al-LDH > Rh-TPPTS/Mg_3Ga-LDH > Rh-TPPTS/Zn_2Ga-LDH. Replacement of Al^{3+} for Ga^{3+} in the Mg_3Ga-LDH support resulted in considerable decrease of the catalyst's activity, as it can be seen in Table 4. Since both the Mg_3Al- and Mg_3Ga-LDH supports have similar structure and composition (except for the trivalent metal cation) it can be

Table 4
Comparative results for the 1,4-addition of arylboronic acids using various LDH docked Rh-TPPTS catalyst

Entry	Catalyst	Boronic acid	Product	Yield[a] (%)
1	Rh-TPPTS/Zn_2Al-LDH	**2a**	**3a**	85
2		**2b**	**3b**	80
3		**2c**	**3c**	60
4		**2d**	**3d**	55
5		**2e**	**3e**	–
6	Rh-TPPTS/Mg_3Ga-LDH	**2a**	**3a**	60
7		**2b**	**3b**	64
8		**2c**	**3c**	40
9		**2d**	**3d**	38
10		**2e**	**3e**	–
11	Rh-TPPTS/Zn_2Ga-LDH	**2a**	**3a**	42
12		**2b**	**3b**	35
13		**2c**	**3c**	20
14		**2d**	**3d**	15
15		**2e**	**3e**	–

[a] Isolated yield based on **1**.

suggested that Al^{3+} renders the LDH solid more basic. However, the basicity considered from LDH presumably does not act directly on the product formation as Na_2CO_3 is present and is known to accelerate the reaction [3–8]. The acidic or basic properties of LDHs may modify the electronic properties of the Rh(I) complex which is in a intimate interaction with the LDH layers and therefore influence the reaction outcome. However, more systematic study to identify these effects is required and is in progress. With regard to the Zn-substituted LDH supports it can be seen from the Zn_2Al-LDH based catalyst that replacement of Mg^{2+} by Zn^{2+} resulted in less active catalyst, thus indicating an enhancement of acidic properties of the LDH support due to Zn^{2+}. In addition, the above-observed negative effect of Ga^{3+} (compared to Al^{3+}) can also be identified in the Zn-based LDH samples used as supports of the Rh catalyst. The catalysts were analyzed after reaction to ensure that the high concentration of Na_2CO_3 used in reaction media does not favor any back-exchange of CO_3^{2-} extracting in the solution the Rh-TPPTS complex, which may act as a homogeneous catalysts. No leaching of the immobilized rhodium complex occurred as indicated by ICP-AES analysis of liquids after separation of the used supported catalyst.

The fact that no leaching occurred confirms that the Rh-TPPTS species are well docked via ionic exchange, as was also evident by the various characterization results shown above. This was further confirmed by the catalytic tests of the recycled catalytic samples. After the reaction, the CO_3^{2-} from Na_2CO_3 replaced the nitrate from the structure of LDHs as it was confirmed by FTIR spectra of the spent catalysts. This replacement of the remaining nitrates with carbonates did not have a significant effect on the reaction, according to the subsequent catalytic/recyclability tests. The recyclability tests were performed for the 1,4-addition of 4-methoxyphenylboronic acid (**2a**) to 2-cyclohexen-1-one (**1**) over all four recycled catalysts (Rh-TPPTS/Mg_3Al-LDH, Rh-TPPTS/Zn_2Al-LDH, Rh-TPPTS/Mg_3Ga-LDH, Rh-TPPTS/Zn_2Ga-LDH). As it can be seen from the results of Table 5, the recycled supported catalysts did not exhibit any significant loss of activity. Three successive 1,4-addition reactions were performed, and after each step the catalyst was separated via centrifugation without any additional treatment. Only a slight decrease of the yield was observed after three runs.

Table 5
Recycling tests for the 1,4-addition of 4-methoxyphenylboronic acid to 2-cyclohexen-1-one

No.	Catalyst	Isolated yield		
		Run 1	Run 2	Run 3
1	Rh-TPPTS/Mg_3Al-LDH	98	95	90
2	Rh-TPPTS/Zn_2Al-LDH	85	83	82
3	Rh-TPPTS/Mg_3Ga-LDH	60	58	54
4	Rh-TPPTS/Zn_2Ga-LDH	42	40	35

4. Conclusions

In conclusion, different hydrotalcite-like materials: Mg_3Al-, Mg_3Ga-, Zn_2Al-, and Zn_2Ga-LDH were successfully prepared and used as support for docking the $Rh(TPPTS)_3Cl$ complex. Immobilization of this complex has most probably occurred on the mouth (edges) of tactoids of LDH layers with a partial penetration of individual TPPTS ligands within the galleries resulting also in the formation of two well-ordered, distinct layered phases, as evidenced by XRD. This occurred without any damage in the structure of either LDH or complex itself. The docked complexes were shown to be efficient catalysts in the 1,4-addition of arylboronic acid to 2-cyclohexen-1-one using neat water as a solvent. The support was not spectator in this reaction, with the type of metals in the layer structure playing a role in the activity of the docked catalyst. The most active catalysts proved to be those supported on Mg–Al based LDH samples. Further studies will be directed to improve the structure/composition of the Rh-TPPTS docked LDHs and to find other catalytic applications with this heterogeneous system.

Acknowledgements

CNCSIS-Romania and the Centre National de la Recherche Scientifique (CNRS) are kindly acknowledged for the financial support. KST would like to acknowledge co-funding of part of this work from European Union and General Secretariat for Research and Technology-Hellas via programme EPAN-Bilateral Cooperation between Greece and Romania (2005-2007). COST Action D36 "Molecular structure-performance relationships at the surface of functional materials" and D24 "Sustainable Chemical Processes: Stereoselective Transition Metal-Catalyzed Reactions" are also gratefully acknowledged. We also thank Dr T. Schlama (Rhodia) for a generous gift of the TPPTS ligand.

References

[1] For selected books, see:
(a) P.A. Grieco (Ed.), Organic Synthesis in Water, Blacky Academic and Professional, London, 1998;
(b) C.-J. Li, T.-H. Chan (Eds.), Organic Reaction in Aqueous Media, Wiley & Sons, New York, 1997;
(c) B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, Wiley-VCH, New York, 1998.
[2] For recent reviews, see:
(a) N. Pinault, D.W. Bruce, Coord. Chem. Rev. 241 (2003) 1;
(b) C.-J. Li, Acc. Chem. Res. 35 (2002) 533;
(c) C.-J. Li, T.H. Chan, Tetrahedron 55 (1999) 11149;
(d) A. Lubineau, J. Auge, in: P. Knochel (Ed.), Modern Solvent in Organic Synthesis, Topics in Current Chemistry, vol. 206, Springer, Berlin, 1999, p. 1;
(e) D. Sinou, in: P. Knochel (Ed.), Modern Solvent in Organic Synthesis, Topics in Current Chemistry, vol. 206, Springer, Berlin, 1999, p. 41;
(f) A. Lubineau, J. Auge, Y. Queneau, Synthesis (1994) 741;
(g) W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524.
[3] (a) M. Sakai, H. Hayashi, N. Miyaura, Organometallics 16 (1997) 4229;
(b) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, J. Am. Chem. Soc. 120 (1998) 5579.
[4] Rh-catalyzed 1,4-addition:
(a) T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, J. Am. Chem. Soc. 124 (2002) 5052, and references cited therein;
(b) R. Amengual, V. Michelet, J.-P. Genet, Tetrahedron Lett. 43 (2002) 5905, and references cited therein.
[5] Asymmetric 1,4-addition to enones.
(a) T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, J. Am. Chem. Soc. 125 (2003) 11508;
(b) C. Debfieber, J.-F. Paquin, S. Serna, E.M. Carrreira, Org. Lett. 6 (2004) 3873;
(c) Y. Otamaru, K. Okamoto, R. Shintani, T. Hayashi, J. Org. Chem. 70 (2005) 2503;

(d) R. Amengual, V. Michelet, J.-P. Genet, Synlett (2002) 1791;
(e) S. Sakuma, M. Sakai, R. Itooka, N. Miyaura, J. Org. Chem. 65 (2000) 5951;
(f) T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara, J. Am. Chem. Soc. 121 (1999) 11591;
(g) S. Sakuma, N. Miyaura, J. Org. Chem. 66 (2001) 8944;
(h) T. Hayashi, T. Senda, M. Ogasawara, J. Am. Chem. Soc. 122 (2000) 10716;
(i) Y. Takaya, M. Ogasawara, T. Hayashi, Tetrahedron Lett. 39 (1998) 8479;
(j) Y. Takaya, T. Senda, H. Kurushima, M. Ogasawara, T. Hayashi, Tetrahedron: Asymmetry 10 (1999) 4047;
(k) Y. Takaya, M. Ogasawara, T. Hayashi, Tetrahedron Lett. 40 (1999) 6957;
(l) Y. Takaya, M. Ogasawara, T. Hayashi, Chirality 12 (2000) 469;
(m) S. Sakuma, N. Miyaura, J. Org. Chem. 66 (2001) 6852;
(n) M. Reetz, D. Moulin, A. Gosberg, Org. Lett. 3 (2001) 4083;
(o) M. Kuriyama, K. Tomioka, Tetrahedron Lett. 42 (2001) 921.

[6] 1,2-addition to aldehydes:
(a) M. Sakai, M. Ueda, N. Miyaura, Angew. Chem. Int. Ed. 17 (1998) 3279;
(b) M. Ueda, N. Miyaura, J. Org. Chem. 65 (2000) 4450;
(c) A. Frustner, H. Krause, Adv. Synth. Catal. 343 (2001) 343.

[7] Friedel Crafts acylation with organoboron reagents:
C.G. Frost, K.J. Wadsworth, Chem. Commun. (2001) 2316.

[8] Y. Otamaru, T. Senda, T. Hayashi, Org. Lett. 6 (2004) 3357.

[9] For acidic clays:
(a) K. Ebitani, T. Kawabata, T. Mizugaki, K. Kaneda, Green Chem. 2 (2000) 157;
(b) T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 42 (2001) 8329;
(c) T. Kawabata, K. Mizugaki, K. Ebitani, Kaneda, J. Am. Chem. Soc. 125 (2003) 10486;
(d) T. Kawabata, M. Kato, T. Mizugaki, K. Ebitani, K. Kaneda, Chem. Lett. 32 (2003) 648;
(e) T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 44 (2003) 9205.

[10] For basic clays:
(a) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Org. Chem. 65 (2000) 6897;
(b) K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 126 (2004) 5662.

[11] For typical catalysis of hydrotalcites as solid bases:
(a) B.M. Choudary, M.L. Kantam, B. Kavita, C.V. Reddy, K.K. Rao, F. Figueras, Tetrahedron Lett. 39 (1998) 3555;
(b) T. Honma, M. Nakajo, T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 43 (2002) 6229.

[12] For typical heterogeneous metal catalysts based on HT:
(a) T. Nishimura, N. Kakiuchi, M. Inoue, S. Uemura, Chem. Commun. (2000) 1245;
(b) B.M. Choudary, N.S. Chowdary, S. Madhi, M.L. Kantam, Angew. Chem. Int. Ed. 40 (2001) 4619.

[13] (a) F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173;
(b) V. Rives (Ed.), Layered Double Hydroxides: Present and Future, Nova Sci. Pub., Inc., New York, 2001.

[14] (a) B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. Kirsh-De Messmacker, P.A. Jacobs, Nature 400 (1999) 855;
(b) B. Sels, D. De Vos, P.A. Jacobs, Catal. Rev. 43 (2001) 443;
(c) B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. 124 (2002) 14127;
(d) A.E. Palomares, J.G. Prato, F. Rey, A. Corma, J. Catal 221 (2004) 62.

[15] (a) N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, J. Org. Chem. 66 (2001) 6620;
(b) B.M. Choudary, N.S. Chowdari, J. Karangula, M.L. Kantam, J. Am. Chem. Soc. 124 (2002) 5341;
(c) M.L. Kantam, B. Choudary, C.V. Reddy, K.K. Rao, F. Figueras, Chem. Commun. (1998) 1033.

[16] (a) A.M. Argo, J.F. Odzak, F.S. Lai, B.C. Gates, Nature 415 (2002) 623;
(b) A. Suzuki, T. Yamaguchi, T. Chibara, Y. Inada, M. Yuasa, M. Abe, M. Nomura, Y. Iwasawa, J. Phys. Chem. B. 108 (2004) 5609.

[17] (a) B.M. Choudary, M.L. Kantam, N.M. Reddy, N.M. Gupta, Catal. Lett. 82 (2002) 79;
(b) B.M. Choudary, B. Kavita, N.S. Chowdari, B. Sreedhar, M.L. Kantam, Catal. Lett. 78 (2002) 373;
(c) J. Huang, T. Jiang, B. Han, T. Mu, Y. Wang, X. Li, H. Chen, Catal. Lett. 98 (2004) 225;
(d) M.L. Kantam, B.V. Prakash, C.R.V. Reddy, B. Sreedhar, Synlett (2005) 2329;
(e) M.B. Choudary, M. Roy, S. Roy, M.L. Kantam, J. Mol. Catal. A 241 (2005) 2009;
(f) B.M. Choudary, M. Roy, S. Roy, M.L. Kantam, Adv. Synth. Catal. 347 (2005) 215;
(g) M.L. Kantam, M.S. Subhas, R.M. Sarabindu, Synlett (2006) 633;
(h) B.M. Choudary, T. Ramani, H. Maheswaran, L. Prashant, K.V.S. Ranganath, K.V. Kumar, Adv. Synth. Catal. 348 (2006) 493;
(i) H. Zhou, G.L. Zhou, X.Z. Jiang, J. Mol. Catal. A: Chem. 248 (2006) 26;
(j) S. Bhattacharjee, J.A. Anderson, J. Mol. Catal. A: Chem 249 (2006) 103;
(k) C. Jiminez-Sanchidrian, M. Mora, J.R. Ruiz, Catal. Commun. 7 (2006) 1025;
(l) D. Tichit, C. Gerardin, R. Durand, B. Coq, Topics Catal. 39 (2006) 89.

[18] (a) H.C. Greenwell, W. Jones, D.N. Stamires, P. O'Connor, M. Brady, Green Chem. 8 (2006) 1067;
(b) D. Tichit, M. De Jesus Martinez Ortiz, D. Francova, C. Gerardin, B. Coq, R. Durand, F. Prinetto, G. Ghiotti, Appl. Catal. A: Gen. 318 (2007) 170;
(c) D. Francova, N. Tanchoux, C. Gerardin, P. Trens, F. Prinetto, G. Ghiotti, D. Tichit, B. Coq, Microporous Mesoporous Mater. 99 (2007) 118;
(d) K.M. Parida, N. Baliarsingh, B.S. Patra, J. Das, J. Mol. Catal. A: Chem. 267 (2007) 202;
(e) M.L. Kantam, P. Srinivas, K.B.S. Kumar, R. Trivedi, Catal. Commun. 8 (2007);
(f) A. Dubey, Green Chem. 9 (2007) 424;
(g) F. Iosif, V.I. Parvulescu, M.E. Perez Bernal, R.J. Ruano-Casero, V. Rives, K. Kranjc, S. Polanc, M. Kocevar, E. Genin, J.-P. Genet, V. Michelet, J. Mol. Catal. A: Chem. 276 (2007) 34;
(h) T. Wongkerd, A. Luengnaruemitchai, S. Jitkarnka, Appl. Catal. B: Environ. 78 (2008) 101;
(i) G. Wu, X. Wang, J. Li, N. Zhao, W. Wei, Y. Sun, Catal. Today 131 (2008) 402;
(j) C. Gerardin, D. Kostadinova, B. Coq, D. Tichit, Chem. Mater. 201 (2008) 2086.

[19] N. Fujita, K. Motokura, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, Tetrahedron Lett. 47 (2006) 5083.

[20] D. Tichit, M.H. Lhouty, A. Guida, B.H. Chiche, F. Figueras, A. Auroux, D. Bartalini, E. Garrone, J. Catal. 151 (1995) 50.

[21] V. Rives, Mater. Chem. Phys. 75 (2002) 19.

[22] M.A. Aramendia, Y. Aviles, J.A. Benitez, V. Borau, C. Jimenez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Microporous Mesoporous Mater. 29 (1999) 319.

[23] A.V. Radha, P.V. Kamath, C. Shivakumara, J. Phys. Chem. B 111 (2007) 3411.

[24] G.S. Thomas, P.V. Kamath, Solid State Sci. 8 (2006) 1181.

[25] J. Coates, Interpretation of infrared spectra, a practical approach, in: R.A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester, 2000, pp. 10815–10837.

[26] V.I. Nefedov, Koord. Khim. 4 (1978) 1285.

[27] (a) E.G. Kuntz, ChemTech (1987) 570;
(b) W.A. Herrmann, J.A. Kulpe, J. Kellner, H. Riepl, H. Bahrmann, W. Konkol, Angew. Chem., Int. Ed. Engl. 29 (1990) 391;
(c) V. Michelet, M. Savignac, J.-P. Genêt, in: L. Paquette, P. Fuchs, D. Crich, P. Wipf (Eds.), Electronic Encyclopedia of Reagents for Organic Synthesis, John Wiley & Sons, New York, 2004.