JOURNAL OF
Materials
CHEMISTRY

Intracrystalline alkylation of benzoate ions into layered double hydroxides

Vanessa Prévot, Blanca Casal and Eduardo Ruiz-Hitzky*

Instituto de Cienca de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain.
E-mail: eduardo@icmm.csic.es

Received 20th June 2000, Accepted 27th September 2000
First published as an Advance Article on the web 1st December 2000

Several layered double hydroxides (LDHs) containing metals of different nature intercalated with benzoate anions have been synthesised in order to study the O-alkylation reaction of the interlayered species with alkyl halide in dry media conditions. In all the cases, the expected ester was obtained with good yield ($>60\%$). The presence of anionic benzoate in the structure was prefered to obtain high selectivity and yield, in comparison with the use of sodium benzoate supported as a salt. The use of MW irradiation to promote these reactions has permitted the reaction time to be reduced considerably. The influence of water present in the LDH on the ester formation has also been investigated. Characterisation of the LDH support before and after reaction is also presented, showing the influence of the nature of the cations located in the octahedral sheets. The support can be regenerated, with no effect on the reactivity.

Introduction

Nowadays, the chemistry community is under increasing pressure to change current working practices in order to find greener alternatives in chemical production. In this way, the application of inorganic reagents in solvent-free media, which involves milder conditions, easier work up and higher selectivity, has rapidly increased. The use of environment-friendly solid acid or base catalysts in dry media conditions, *i.e.* without any solvent, appears as one promising solution to reduce the amount of toxic wastes and by-products arising from chemical processes.

The thermal energy source provided by microwave (MW) irradiation is more and more used in organic synthesis because of the following main advantages: high reaction rates, excellent yields with minimisation of by-products and ease of utilisation.[1] We have reported[2] the interest in combining both solvent free media and MW activation for different type of reactions (*e.g.* alkylation reactions) using inorganic solids, such as alumina, as the support. This was extended to a great variety of reactions involving the use of different inorganic solids.[3] More recently, we have shown the application of this methodology to the synthesis of herbicides, consisting of the esterification of 2,4-dichlorophenoxyacetic acid (2,4-D) using microparticulated solids such as clays, silica and other oxides as reaction supports.[4]

The special topology of certain solids (2D) allows intracrystalline reactions in which the control of the diffusion mechanism of the reactants imposed by the structural nature of the solids could strongly determine both the yield and selectivity of the reaction.[5] So nucleophilic substitution reaction and alkylcyanide synthesis have been described involving interlayered anions of layered double hydroxides (LDHs).[6,7] The LDHs are lamellar compounds with a structure derived from the brucite type $M^{II}(OH)_2$, where trivalent metallic cations such as Al, Cr, Fe, Ga, V, *etc.*[8–10] replace some of the divalent ones (Mg, Zn, Cu, Ni, Co, Mn, *etc.*) creating a net positive charge on the layers $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$. Overall electroneutrality is obtained by the intercalation of inorganic or organic anions into the interlamellar space $[A^{y-}_{x/y}\cdot nH_2O]^{x-}$. According to the fields of application, a wide range of derivatives containing various combinations of M^{II}, M^{III} and A (henceforth abbreviated M^{II}–M^{III}–A) can be synthesised either directly or by anionic exchange, the main property of these materials being their anionic exchange ability. Catalysis is the predominant field of application for these materials,[11,12] which are principally used as precursors of finely divided mixed metallic oxides. In a preliminary study, we have recently reported[13] that carboxylates intercalated into a ZnCr matrix $[Zn_2Cr(OH)_6]^+(C_6H_5CO_2^-)$ are alkylated in dry media with good yields, activating the reaction by heating either in a conventional furnace or in a domestic MW oven.

This paper reports the synthesis of alkylbenzoates using benzoate intercalated into LDHs with different compositions (eqn. 1) in order to investigate the influence of the nature of the cations located in the octahedral sheets as well as to enlarge the potential uses of this class of layered matrices (Scheme 1).

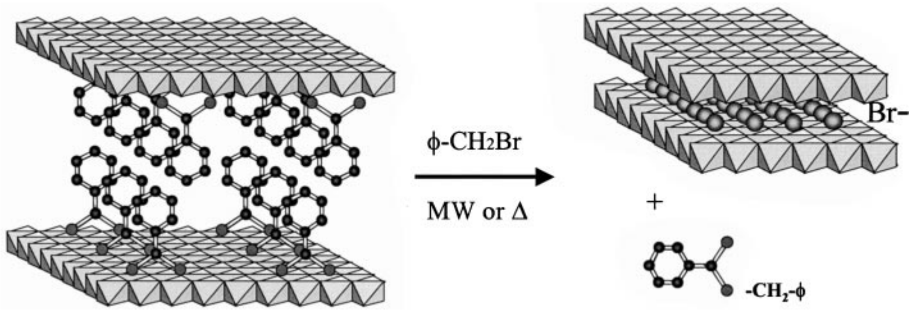
$$\begin{aligned}&[\mathrm{LDH}]\text{-benzoate}+C_6H_5\text{-}CH_2\text{-}X\\&\rightarrow[\mathrm{LDH}]\text{-}X+C_6H_5CO_2\text{-}CH_2\text{-}C_6H_5\end{aligned}\qquad(1)$$

Some reactions were also carried out using LDH chlorides as reaction supports impregnated with sodium benzoate, in order to compare the behaviour of these systems with the similar reactions using the confined benzoate (as exchangeable anion). We have also studied the influence of different parameters on the esterification such as the hydration degree of the matrix and the alteration of the support after the thermal decomposition during the synthesis.

Experimental

Starting materials

All chemicals were purchased from Aldrich. LDHs containing chloride ions were prepared using well established methods.[8,10] $[Zn_2Al(OH)_8]$-, $[Zn_2Cr(OH)_6]$-, $[Mg_2Al(OH)_6]$-, and $[Co_2Al(OH)_6]$-LDHs, denoted as ZnAl, ZnCr, MgAl and CoAl, with an M^{II}/M^{III} ratio close to 2 were prepared by coprecipitation at controlled pH. In this way, 50 ml of a mixed metal chloride solution having total cation concentrations of 1 M with the expected M^{II}/M^{III} molar ratio were used and the pH was maintained during coprecipitation by the simultaneous



Scheme 1 Schematic representation of the intercrystalline alkylation reaction.

addition of an aqueous solution of NaOH (1 M). Values of pH of coprecipitation are imposed by the nature of the LDH matrices: pH 8.0 for ZnAl, 4.5 for ZnCr, 11.0 for CoAl, and pH 9.5 for MgAl. The synthesis was performed under nitrogen to prevent contamination by carbonate from atmospheric CO_2. The reaction mixtures were aged for 36 h and the resulting precipitates were recovered after three dispersion and centrifugation consecutive cycles. Finally, the solids were air dried.

$[Cu_2Cr(OH)_6]$-LDH, denoted as CuCr-Cl, was prepared by reacting solid CuO in a 5% aqueous suspension with a 1 M solution of $CrCl_3{\cdot}6H_2O$ under vigorous stirring at room temperature.[8] The addition of chromium chloride was carried out very slowly (2 μl min^{-1}). The precipitate was allowed to stand during one week, the pH remaining constant at 4.5. After such time, the solid was recovered by centrifugation, water washed and air dried.

Intercalation of benzoate (BC) ions

About 1 g of LDH was dispersed in 75 ml of an aqueous solution containing a ten fold molar excess of sodium benzoate per M^{III} and was allowed to react during 24 h under continuous stirring and nitrogen flow. The pH of the solutions was adjusted in a similar way to that described for the coprecipitation of the precursor.

Recycled matrix: the compound collected after reaction was submitted to exchange reaction as described above. The intercalated compound was water washed and air dried, being used again in further alkylation reactions.

Direct coprecipitation

The method of coprecipitation at constant pH was used to obtain the CoAl-BC compound. 20 ml of a mixed Co/Al chloride solution containing 0.02 mole of total metal and with a Co/Al ratio of 2 were added dropwise to 75 ml of a 0.5 M benzoate solution. The pH was maintained during the reaction at a value of 11.0 by slow addition of 1 M NaOH (aq). The reaction mixture was aged at room temperature for 36 h under nitrogen. The resulting slurry was centrifuged, repeatedly washed with deionised water and air dried at room temperature.

Alkylation reactions

For the LDH-BC intercalated solids, 0.1 g of the compound was impregnated with stoichiometric amounts of the selected alkyl halide, and placed in a Teflon reactor. For LDHs that were used only as a reaction support, sodium benzoate and 0.1 g of the LDH chloride precursors were intimately mixed in stoichiometric proportions and impregnated with the alkyl halide as described above.

The reaction mixture was heated over variable periods of time (30 min to 12 h) in an oven at 100 °C. Alternatively the heating was carried out by MW irradiation (160–900 W, 1–20 min). In all the cases, the resulting products that remained impregnated on the solid support were extracted with methanol, filtered and analysed by GC-MS.

The experiments using MW irradiation (2450 MHz) were carried out in a domestic Moulinex FM 460 oven. Under the adopted conditions, the temperature never exceeded 150 °C. Characterisation of the extracted phases after reaction was carried out by GC-MS using a Hewlett Packard 5890 series II chromatograph coupled to a selective mass detector series 5971 equipped with a capillary column (25 m length and 0.20 mm internal diameter), with a stationary phase (methylsilicone) of 0.33 mm thickness.

Characterization techniques

Powder X-ray diffraction (PXRD) data were obtained using a Philips PW 1710 diffractometer with Cu-Kα radiation with a Ni filter. An FTIR Nicolet 20SXC spectrophotometer was used to obtain the corresponding IR spectra from the samples dispersed in KBr (pellets). Thermogravimetric analysis (TGA) were carried out using a Setaram TG-DTA92 thermogravimetric analyzer, from room temperature to 1050 °C in air atmosphere with a temperature ramp rate of 5 °C min^{-1}.

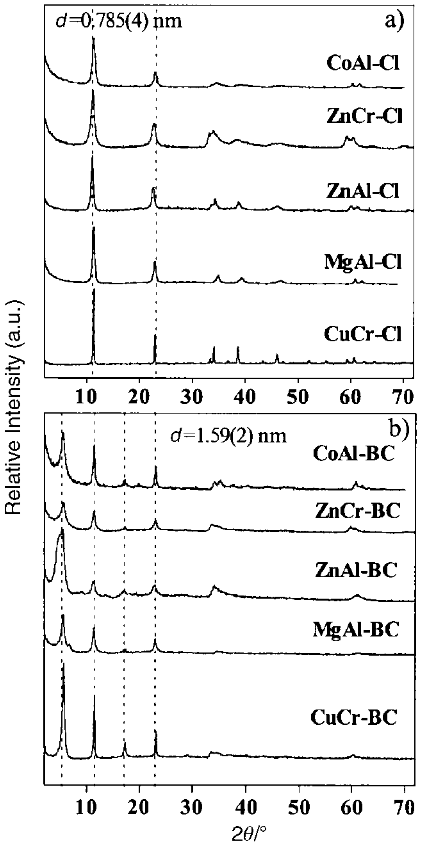


Fig. 1 PXRD patterns of the precursor LDHs (a) and benzoate intercalated LDHs (b) used for the O-alkylation of benzoate.

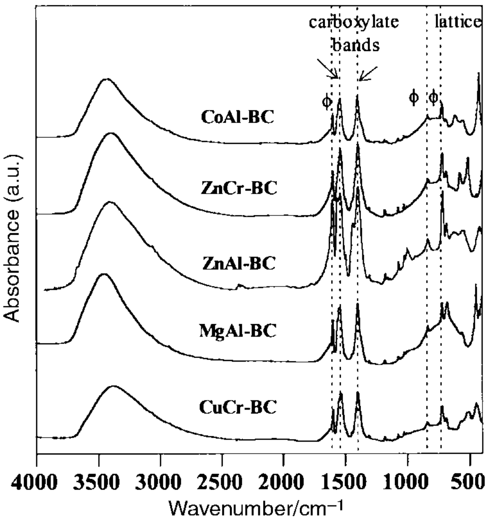


Fig. 2 FTIR spectra of the benzoate intercalated into the LDHs used for the O-alkylation reactions.

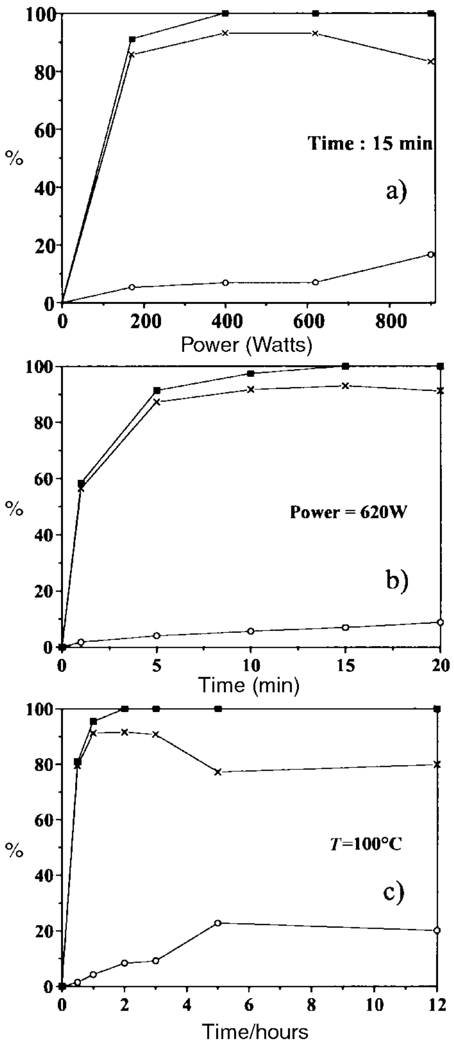


Fig. 3 Evolution of the benzoate O-alkylation reaction using ZnCr-BC matrix: a) under conventional thermal treatment for 15 min at different microwave powers, b) under microwave activation at 620 W and c) using conventional heating at 100 °C. Legend: Square for conversion, cross for expected ester benzylbenzoate and open circle for the by-product, 1,1′-[oxybis(methylene)]bisbenzene.

Chemical analyses were performed at the Vernaison Analysis center of CNRS (France). Scanning electron micrographs were recorded with a Cambridge Stereoscan at the Laboratoire des Materiaux Inorganiques of Techinauv S.A., France.

Results and discussion

LDH benzoate (LDH-BC) starting materials

Newman and Jones[14] reviewed recently the different methods for preparing organo-LDHs. In our case, the direct anion exchange procedures described in the experimental section were successfully applied in most of the LDH-BC samples here prepared. In the case of the CoAl matrix, the standard anion exchange conditions did not give rise to the expected intercalated compound. This one was finally obtained by the direct coprecipitation method reported in the experimental section.

Powder X-ray diffraction PXRD patterns of chloride precursors and LDH-BC compounds are presented in Fig. 1. All the diagrams display the characteristic diffraction peaks assigned to the matrix LDH structures in agreement with a complete intercalation of benzoate ions between the LDH layers. Similar basal spacing values (1.59 ± 0.02 nm) are obtained for all the LDH-BC phases after benzoate intercalation, corresponding to single layer arrangements of benzoate ions, in the LDH interlayer spaces as already described.[15,16]

The effective intercalation of benzoate in the LDHs has been confirmed by infrared spectroscopy (Fig. 2). So, the characteristic bands of the carboxylate function, *i.e.* the $\nu_{\mathrm{as(coo\text{-})}}$ and $\nu_{\mathrm{s(coo\text{-})}}$ bands, in the 1600–1300 cm^{-1} region and the phenyl group vibration bands at 717 cm^{-1}, 844 cm^{-1} and 1605 cm^{-1} are clearly observed.

Reactions of LDH-BC with alkyl halides

In a preliminary set of experiments, the O-alkylation of ZnCr-BC was attempted using benzyl compounds such as benzyl chloride, benzyl bromide and benzyl alcohol. Under 15 min of MW irradiation at 600 W, only the benzyl bromide acts as an efficient reagent allowing the formation of the expected ester with a significant reaction yield (93%). Conventional thermal activation permits also a high conversion rate using the alkyl bromide with approximately the same yield (92%). In an opposite way, the esterification process was not observed when benzyl chloride was used in place of benzyl bromide. Only a small amount of such reagent (23%) reacts to give benzoic acid when the reaction mixture is MW irradiated. Nevertheless the selective formation of benzylbenzoate with a yield of 76% is obtained for experiments carried out under conventional heating. It is well known that in organic synthesis, chloride alkylating agents are usually less reactive than their corresponding bromides,[2] and this result points out that the use of MW activation increases this difference in their reactivity. This high reactivity of benzyl bromide compared to the chloride induces also the formation of a condensation by-product: 1,1′-[oxybis(methylene)]bisbenzene, not observed in the case of benzyl chloride.

Any O-alkylation reaction occurs in the presence of benzyl alcohol, indicating that the mechanism of ester formation in the presence of benzyl halides does not involve such a hydroxy compound as intermediate. Note that LDH solids exhibit a marked basic character associated with the reactive OH groups, which could tentatively be involved in halide substitution reactions.

The O-alkylation of the intercalated benzoate by benzyl bromide was tested for different times under conventional thermal activation or MW irradiation, as well as for different powers of irradiation (between 170 W and 900 W) (Fig. 3). When the MW powder was greater than 400 W total conversion was obtained for 15 min of irradiation (Fig. 3a). Thus, we fixed the MW oven power at 620 W. After only 1 min of irradiation 60% of benzyl bromide had reacted and total conversion occurred after 15 min of irradiation (Fig. 3b). As usually takes place in MW assisted reactions using solid supports, we observed that the use of MW irradiation considerably reduces the reaction time in comparison with conventional heating at 100 °C.[1,3] In these last conditions, two hours were necessary in order to observe total conversion (Fig. 3c). It is interesting to note that the yield of benzoate ester is slightly reduced with the use of higher power (900 W) or overheating, with a concomitant increase of the condensation by-product.

It is noteworthy that the use of LDH chloride precursors, in comparison with LDH nitrate precursors, induces better selectivity, preventing the formation of benzyl alcohol or benzaldehyde as was observed in a preliminary study.[17] Moreover, in any case we observed the formation of benzyl chloride, that could be hypothetically formed by reaction between residual interlamellar chloride anions and the bromoalkyl compound, in agreement with the observed total exchange of chloride by benzoate.

From the results of the kinetics further experimental conditions adopted for the reactions were: 15 min for MW irradiation at 620 W and 3 h for conventional heating at 100 °C. The esterification reaction of intercalated benzoate was tested with different matrices: $[Zn_2Al(OH)_8]$-, $[Cu_2Cr(OH)_6]$-, $[Mg_2Al(OH)_6]$-, $[Co_2Al(OH)_6]$-LDH, denoted as ZnAl, CuCr, MgAl, CoAl. Total conversions of benzoate and ester yields are presented in Fig. 4. The results obtained from the MgAl-BC and CuCr-BC compounds show a 100% selective synthesis of benzyl benzoate. The conversion is slightly improved when the CuCr matrix is used (100%) compared to MgAl (96%) under MW activation, whereas for the former a yield of 92% is obtained after 3 h in a conventional oven compared to 89% when MgAl-BC was used. Similar results are observed for both ZnCr-BC and CoAl-BC matrices: they display reaction selectivities lower than 100%, but the yields of the ester remain almost at the same values. The lowest yield is observed using ZnAl-BC, in this case the selectivity also strongly decreases.

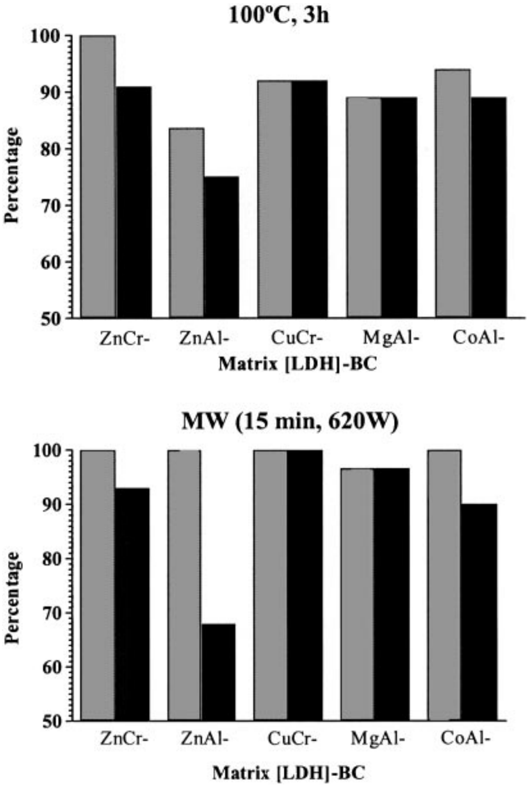


Fig. 4 Conversion (grey) and yield (black) of ester with different benzoate LDHs, top under conventional thermal treatment (3 h at 100 °C), bottom under microwave activation (15 min at 620 W).

The fact that similar results observed for MgAl- are also observed for CuCr-LDH matrices, which display different acid–base and redox properties, evidences that the development of the reaction does not depend on the chemical properties of the LDH sheets. It appears that there is rather a dependence on the diffusion of both interlayer benzoate and organic reagent, as well as on their accessibility to the external surface imposed by the topology of the solids.

The reaction has also been carried out using LDH-chloride like a support in place of a true reagent with the intercalated benzoate ions. In this case, the ZnCr-Cl matrix was used. Total conversion of benzoate was always achieved but the yield of ester decreased to 70% and 61% for activation in a conventional oven and under MW irradiation respectively. It could be assumed that the reaction needs water to promote the dissociation attack of the benzoate salt and to produce partially hydrated and rather active anions on the surface of the LDH. In this way, reduced rate of formation of the ester in comparison with the rate of condensation of the by-product is observed. Also, the reaction can only occur using LDH either as reagent or as support. It is interesting to underline that the yields obtained with LDHs are better than the ones obtained when the esterification reactions of benzoate are supported on alumina. They did not go beyond 65% whatever bromoalkyl was used.[17,18]

Role of water and modification of the matrix

Ando and coworkers[19] have reported that the O-alkylation supported reactions on alumina were facilitated by the presence of water at trace levels. The optimum water amount varies depending on the nature of the alkaline metal cations involved in such reactions. Fig. 5 represents the TG, DTG and DTA curves for the starting ZnCr-BC solid. The decomposition goes through four steps involving: desorption of physically adsorbed water, desorption of interlamellar water, dehydroxylation of the host lattice sheet and, finally, combustion of the organic anion occurring between 315 °C and 420 °C. The ZnCr-BC matrix was heated during 3 h at different temperatures: 100 °C, 150 °C, 200 °C and 300 °C just before the combustion of the organic species. Fig. 6a displays the PXRD diagrams of ZnCr-BC heated at 300 °C compared with the uncalcined phase. At this temperature, the overall LDH structure has collapsed, but the presence of the broad diffusion bands centred at 5° (001), 33° (012) and 58° (110), traduce the formation of a "sandwich structure" in which mineral and organic domains alternate. As such this structure is retained up to the decomposition of the organic matter. The preservation of the lamellar habit is confirmed by the SEM micrographs (Fig. 7), for both the

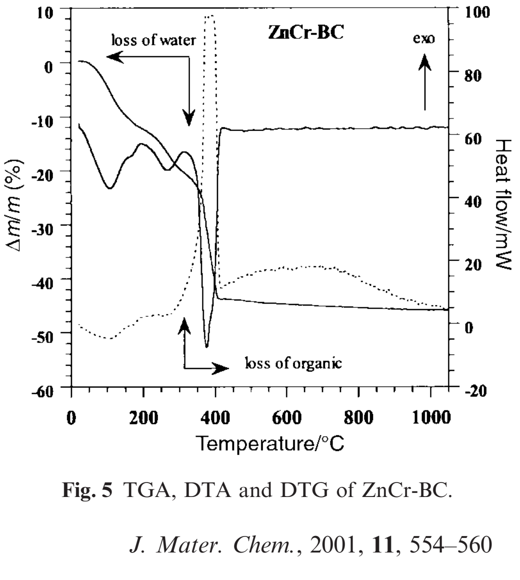


Fig. 5 TGA, DTA and DTG of ZnCr-BC.

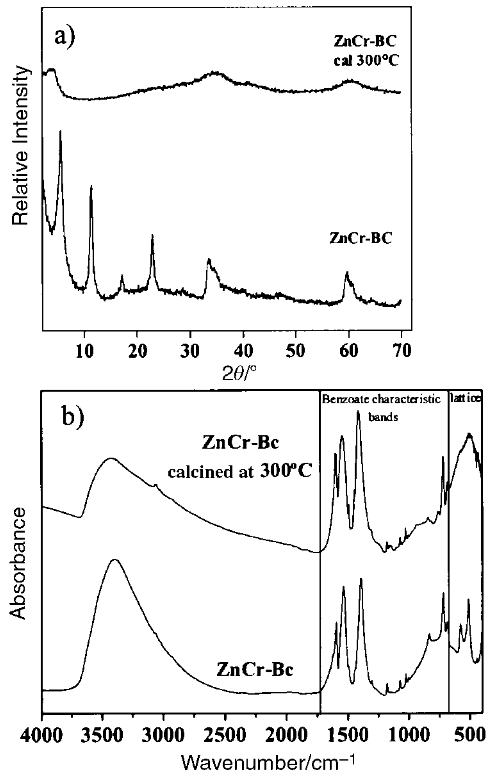


Fig. 6 PXRD patterns (a) and FTIR spectra (b) of uncalcined ZnCr-BC and ZnCr-BC calcined at 300 °C during 3 h.

starting ZnCr-BC matrix and the calcined (300 °C) phase. The presence of the characteristic vibration bands of the carboxylate functions and the phenyl groups in the FTIR spectra of the calcined phase (Fig. 6b), shows the entrapment of the organic species into the inorganic solid. Note also the intensity decrease of the large bands centred at 800 cm^{-1} (M–OH vibration bands) due to the dehydroxylation of the LDH sheet. Strong modification of the lattice vibration indicates the formation of mixed oxides from the LDH solids.

The O-alkylation results obtained from thermally treated LDHs are displayed in Fig. 8. Whatever the thermal energy source, conventional heating or MW irradiation, a preliminary thermal treatment of the LDH-BC induces a decrease in the formation of the ester although the conversion rate remains elevated. It seems for this reaction that the interlayer water facilitates the migration of the benzoate anions to the external edge of the solid and to the reactive surface sites. This ability could explain the good yield obtained from the untreated ZnCr-BC. Nevertheless, pre-treatment of ZnCr-BC at 150 °C gives rise to a better ester yield than pre-treatment at 100 °C, so the ester formation does not directly correlate to the water content. In this case, the total removal of adsorbed water by thermal treatment at 150 °C, which permits the enhancement of the alkyl halide adsorption on the LDH surface,[6] appears to be a compromise with the lack of water, and could explain the observed reaction yield.

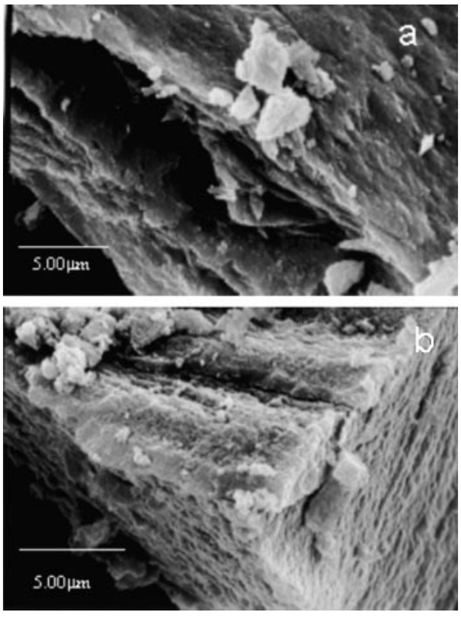


Fig. 7 SEM images for a) ZnCr-Bc uncalcined and b) ZnCr-BC calcined at 300 °C during 3 h.

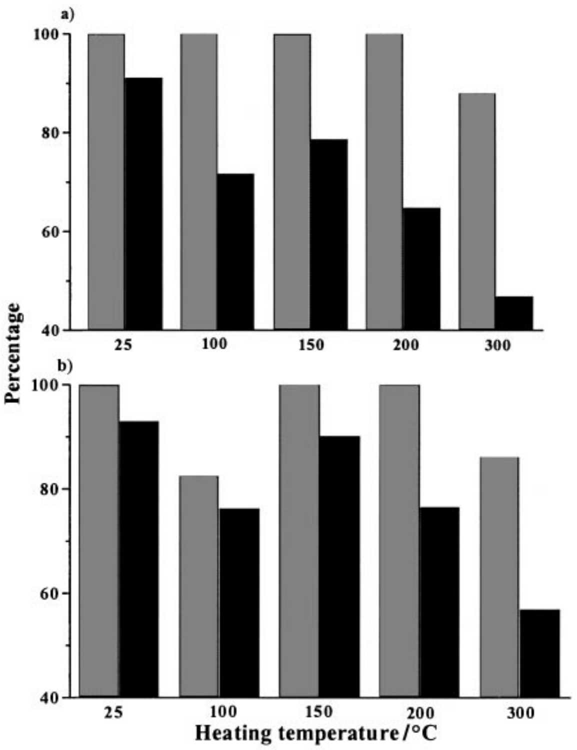


Fig. 8 Percentage of conversion (grey) and of expected ester (black) using ZnCr-BC matrix preliminary heated at different temperatures a) under conventional thermal treatment, b) under microwave activation.

After dehydroxylation (300 °C), the conversion and the yield of benzylbenzoate decreases to a considerable extent. The benzoate appears to be less accessible or less mobile into this "sandwich structure" described above. It could be assumed that the mobility of the species inside such a structure is strongly limited due to the total absence of water and to the decrease of a large extent of the OH groups. In this situation only the organic anions located on the crystal edges and on the external surface of the solid could be able to react with the alkyl halide species.

Reusability of the inorganic matrices

PXRD patterns of different matrices after reaction under MW irradiation are collected in Fig. 9a. Similar diagrams were obtained for the same solids activated by conventional thermal treatment. In all the cases, these results confirm the preservation of the hydrotalcite-like structure. While the benzoate intercalated phases display basal spacings around 1.59 nm, after reaction the resulting compounds present a small basal spacing of 0.78 ± 0.02 nm. We note an inversion of intensity of the two first 001 diffraction lines. This has been observed for LDHs containing heavy interlayer anions, in particular bromide anions.[20] So the diminution of the basal spacing can be explained by the exchange of the benzoate anion by bromide ions in the interlayer region of the solid during the reaction

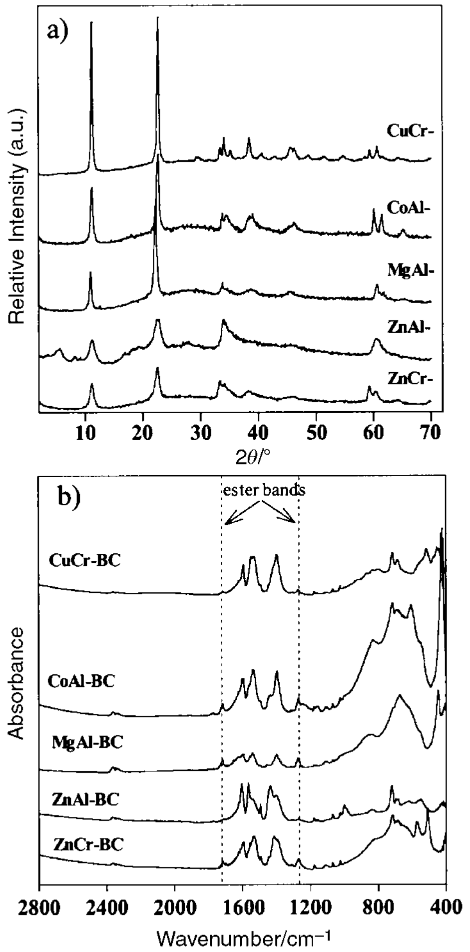


Fig. 9 Benzoate intercalated LDH compounds after alkylation reactions: a) PXRD patterns and b) FTIR spectra.

process. Elemental chemical analyses (Table 1) of the ZnCr matrix confirmed the presence of bromide anions in the resulting compounds. The ratio Zn^{II}/Cr^{III}, which was preserved during the anionic exchange of the chloride precursors with the benzoate anions, decreases after reaction with the bromoalkyl compound. This slight change in composition could be related to the observed changes in the XRD patterns indicating the formation of the amorphous phase in the diagrams between 15° and 35° (2θ) (Fig. 10). During the reaction due to the thermal treatment, a little amount of amorphous ZnO is formed. In the case of the ZnAl matrix only, the diagram after reaction presents characteristic diffraction peaks of unreacted ZnAl-benzoate. In this case, a part of the intercalated benzoate anions has not reacted, thus explaining the relatively low yield of ester (76%) obtained from this matrix (microwave activation). For all the other phases, PXRD patterns show diffraction peaks of pure bromide-LDH phases. However, the use of IR spectroscopy, which is a more sensitive technique, always shows the presence of carboxylate vibration bands in the 1600–1300 cm^{-1} region (Fig. 9b), as well as low intensity absorption bands at 1272 and 1711 cm^{-1}, which correspond to ν_{C-O} and $\nu_{C=O}$ vibrations of the resulting ester, that remains adsorbed on the LDH matrix. Such a technique confirmed the retention of the lattice characteristic vibrations in the 800–400 cm^{-1} region too. Note that the thermal activation necessary to carry out the reaction, whatever the source, does not affect the structural arrangement of the starting host lattice.

Table 1 Chemical ratios in ZnCr-LDH solids

Matrix	Zn/Cr	BC/Cr	Cl/Cr	Br/Cr	H_2O/Cr
ZnCr-Cl	2.0	—	1.08	—	2.2
ZnCr-BC	1.9	0.99			2.3
ZnCr-[a]	1.8	—	—	0.89	2.5

[a] After reaction with benzyl bromide under MW irradiation.

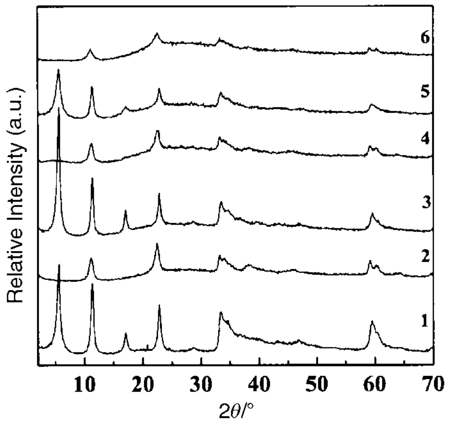


Fig. 10 PXRD patterns of ZnCr during three cycles of O-alkylation reaction. 1) ZnCr-BC, 2) ZnCr-BC after first reaction with bromobenzyl, 3) phase 2 after anionic exchange with benzoate, 4) phase 3 after reaction, 5) phase 4 after anion exchange with benzoate and 6) phase 5 after the third O-alkylation reaction.

Table 2 Results of successive O-alkylation reactions using ZnCr-BC

	1st Cycle	2nd Cycle	3rd Cycle
Conversion (%)	100	93.6	94.2
Ester (%)	93.0	86.3	89.1
By-product[a] (%)	7.0	7.3	5.9

[a] 1,1′-Oxybis(methylene)bisbenzene.

The reusability of the LDH compounds was tested on ZnCr-BC. Fig. 10 presents the PXRD patterns of the recycled supports. After three cycles, the LDH structure is always preserved, the diagrams display characteristic diffraction peaks of successive phases intercalated either as benzoate or as bromide ions. Nevertheless, we note a decrease in the crystallinity of the compounds: the diffraction peaks become larger and a loss of their intensity appears during successive cycles. The corresponding yields obtained are reported in Table 2. It can be assumed that their activity is little modified by the use of recycled LDH matrices.

Conclusion

O-Alkylation reaction of benzoate is performed with both benzoate intercalated ZnCr LDH and benzoate sodium salt supported on an LDH matrix under MW irradiation or classic thermal treatment. In either case, the formation of the expected ester is always observed with yields higher than 60%. Nevertheless, the use of intercalated LDH-benzoate, where the anions are located within the lamellar structure of the inorganic host lattice, improved the yield. This behaviour is also observed after pre-thermal treatment of this intercalated matrix at 150 °C. Selective reaction, without formation of condensation by-products, is carried out when CuCr-BC and MgAl-BC are selected as host lattices. After reaction, the collected compounds correspond to bromide intercalated LDHs, which can be used again without significant loss of their activity. Successive reactions on the same recycled support give rise to similar yields (around 80%). We assumed that the reaction occurs on the external edge surface *via* migration of the interlayer species. Nevertheless, the reaction of the total amount of interlayered benzoate might suggest the accessibility of the interlayered space of LDH, which could then be considered like a nanoreactor, opening the way to new reactions involving anionic intercalated species.

Acknowledgements

This work was partially supported by the CICYT (Spain). V. Prevot thanks the Conseil Regional of Auvergne (France) for a postdoctoral fellowship. The authors gratefully acknowledge technical assistance from J. Merino and M. A. Muro (ICMM) and from V. Ravel and A. M. Mafille, from Techinauv, who recorded the SEM micrographs. We also thank A. L. Garcia-Ponce for helpful discussions.

References

1 (*a*) *Microwave Enhanced Chemistry. Fundamentals, Sample Preparation and Applications*, ed. H. M. Kingston and J. Haswell, American Chemical Society, Washington, DC, 1997; (*b*) D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1.

2 (*a*) E. Gutierrez, A. Loupy, G. Bram and E. Ruiz-Hitzky, *Tetrahedron Lett.*, 1989, **30**, 945; (*b*) G. Bram, A. Loupy, M. Majdoub, E. Gutierrez and E. Ruiz-Hitzky, *Tetrahedron*, 1990, **46**, 5167.

3 R. S. Varma, *Green Chem.*, 1999, **1**(1), 43.

4 L. Lami, B. Casal, L. Cuadra, J. Merino, A. Alvarez and E. Ruiz-Hitzky, *Green Chem.*, 1999, **1**(4), 199.

5 J. M. Thomas and W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997.

6 E. Suzuki, A. Inoue and Y. Ono, *Chem. Lett.*, 1998, 1291.

7 K. J. Martin and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1986, **108**, 541.

8 A. de Roy, C. Forano, K. El. Malki and J. P. Besse, in *Anionic Clays: Trends in Pillaring Chemistry, Synthesis of Microporous Materials*, eds. M. L. Occeli and E. R. Robson, Van Nostrand Reinhold, New York, 1992, vol. 2, p. 108.

9 S. Velu and C. S. Swamy, *Appl. Catal.*, 1996, **145**, 141.

10 W. T. Reichle, *J. Catal.*, 1985, **94**, 547.

11 A. Vaccari, *Catal. Today*, 1998, **41**, 53.

12 F. Malherbe, C. Depege, C. Forano, J. P. Besse, M. P. Atkins, B. Sharma and S. R. Wade, *Appl. Clay Sci.*, 1998, **13**, 451.

13 A. L. Garcia-Ponce, V. Prevot, B. Casal and E. Ruiz-Hitzky, *New J. Chem.*, 2000, **24**, 119.

14 S. P. Newman and W. Jones, *New J. Chem.*, 1998, **22**, 105.

15 M. Meyn, K. Beneke and G. Lagaly, *Inorg. Chem.*, 1990, **29**, 5201.

16 F. Kooli, I. C. Chisen, M. Vucelic and W. Jones, *Chem. Mater.*, 1996, **8**, 1969.

17 P. Lazlo, *Preparative chemistry using supported reagents*, Academic Press, San Diego, 1987.

18 G. Bram, T. Fillebeen-Khan and N. Geraghty, *Synth. Commun.*, 1980, **10**(4), 279.

19 T. Ando, T. Kawate, J. Yamawaki and T. Hanafusa, *Chem. Lett.*, 1982, 935.

20 A. Ennaqadi, Ph.D. Thesis, Université de Clermont-Ferrand, France, 1998.