

Intracrystalline reactivity of layered double hydroxides: carboxylate alkylations in dry media

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This work concerns the reactivity in dry media conditions, i.e. without solvents, of layered double hydroxide (LDH) solids, containing carboxylate ions in their structure, towards alkyl and benzyl halides. Reaction occurs giving the corresponding esters, with excellent yield and selectivity, and preserving the lamellar arrangement of the pristine solids. The reactions were activated by conventional thermal treatment (100 °C) or by microwave (MW) irradiation.

The main novelty of the present contribution is that the process studied is a topotactic reaction, that takes place in the interlayer region of the LDH. In a topotactic reaction the 2D structural arrangement at the solid is preserved after reaction. This differs from conventional anionic activations, which are also promoted under mild conditions but which use inert inorganic solids like alumina¹ or silica² as the “support” of such reactions. The processes reported here are related to anionic activations, but in this case the starting LDH-carboxylates can be regarded as organo-inorganic solids that act as reagents in which the carboxylate is the counter-ion of a bulky macrocation, in this case the bimetallic oxyhydroxy layered framework of the LDH solid. Thus, carboxylates arranged in the interlayer region of these solids are able to react with organic halides, such as 1-bromooctane and benzyl bromide, to produce the corresponding esters and, as a result of the reaction, the LDH interlayer anions are now halide (Br⁻) species in place of the starting RCO₂⁻ ions (Scheme 1).

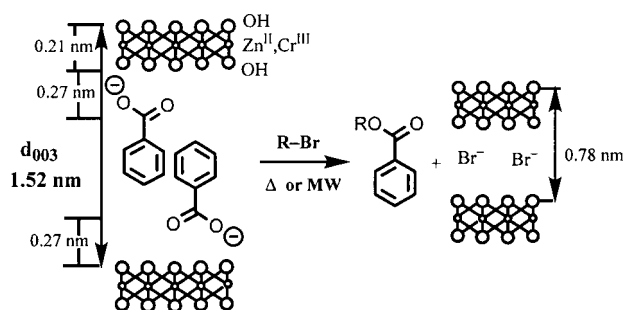
According to Varma,³ the use of inorganic solids for selective organic reactions significantly contributes to the development of a green chemistry for new clean processes. The special topology of certain solids (2D), as layered silicates, some transition metal oxides or even certain phosphonates,⁴ allows intracrystalline reactions in which the control of the diffusion mechanism of the reactants imposed by the structural features of the solids could strongly determine both the yield and the selectivity of such reactions.⁴ Moreover, some of these pro-

cesses present higher yields when the heating is carried out using microwave (MW) irradiation.^{2,5}

In this communication, we report the *O*-alkylation of carboxylate species inherent to LDH materials containing anions such as acetate or benzoate deliberately introduced in the interlayer space as counter-ions of the cationic metal hydroxide sheet. These LDH materials belong to a family of 2D solids known as *anionic clays*, which are currently receiving great attention because of their large field of applications, in particular as precursors of catalysts exhibiting base properties and also as catalyst supports.^{6–10} As indicated above, one of the main salient features presented in this communication is related to the use of such types of solids in topotactic reactions taking advantage of the possibility to select, by an easy ionic exchange process, the nature of the intercalated anions.

In this study we have selected the cationic Zn(II)Cr(III) sheet hydroxides of [Zn₂Cr(OH)₆]⁺[NO₃⁻]⁻·*n*H₂O composition, noted ZnCr-NO₃, which can readily exchange the interlayer nitrate species for other anionic entities.^{9–13} This solid was chosen because of: (i) its low affinity to entrap CO₂ from the atmosphere, avoiding the formation of interlayer carbonate species that are competitive with the selected anions, (ii) its easy and efficient use as an anionic exchanger with a homogeneous distribution of the Zn(II)/Cr(III) in its structure, and (iii) the presence of Cr(III) in the LDH framework that could be used in oxidative processes. Nevertheless, other LDH solids such as, for instance, those derived from ZnAl matrices are also operative for the selected reaction. The exchanged LDH acts as a true reagent where the interlayer carboxylates exhibit enhanced reactivities as required for the alkylation of these species. We have chosen as a model the alkylation of interlayer acetate and benzoate in the reaction with R-CH₂Br (R = C₇H₁₅; C₆H₅) compounds. It must be stressed that these reactions are extremely slow under conventional conditions, i.e. in organic solvents. When working in homogenous media only the addition of crown ethers and quaternary ammonium salts, acting as phase transfer catalysis (PTC) agents, could increase the reaction rates of some anionic activation reactions.¹⁴

The XRD patterns give interlamellar distances of 1.23 and 1.52 nm for the LDH-acetate and LDH-benzoate intercalation compounds, denoted ZnCr-Ac and ZnCr-Bn, respectively (Fig. 1). The intercalation of both anions was also confirmed by FTIR spectroscopy through the presence of the vibrational bands assigned to these organic species. After intercalation, replacement of the ν₅ and ν₂ bands of the nitrate ion by the symmetric (1342 cm⁻¹) and antisymmetric (1556 cm⁻¹) carboxylate stretching bands was observed. For instance, the IR spectrum of ZnCr-Bn (Fig. 2, curve b) clearly shows the 1590 cm⁻¹ band assigned to the phenyl group, in addition to the symmetric and the antisymmetric bands of the carboxylate ions at 1390 and 1532 cm⁻¹, respectively.



Scheme 1 Schematic representation of the intracrystalline reaction of ZnCr-Bn with alkyl bromides giving the corresponding ester and the ZnCr-Br compounds (Bn = benzoate anion).

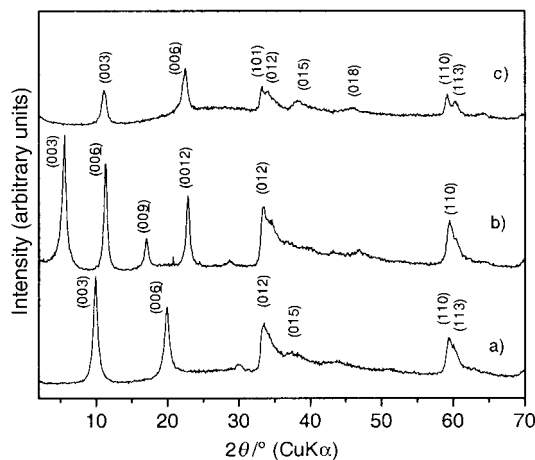


Fig. 1 X-Ray diffraction patterns of (a) ZnCr-NO₃ (precursor), (b) ZnCr-Bn and (c) the resulting product after reaction of ZnCr-Bn with benzyl bromide (MW irradiation).

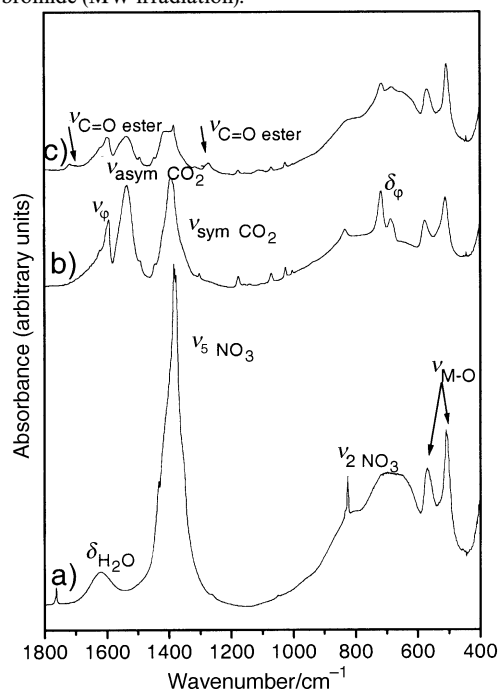


Fig. 2 FTIR spectra of (a) ZnCr-NO₃ (precursor), (b) ZnCr-Bn and (c) the resulting product after reaction of ZnCr-Bn with benzyl bromide (MW irradiation).

As a general rule, under the adopted experimental conditions, good conversion rates were obtained; the yield of ester **2** was generally higher than 70% (Table 1). The development of the reactions strongly depends on the nature of the carboxylate **1**, as well as on the nature of the organic halides **a** and **b**. Depending on the reactants used, different types and ratios of by-products were detected. Thus, the formation of alcohol **3** could be attributed to the basic character of the LDH matrix. The formation of benzaldehyde only took place when the reaction was MW-assisted. We assume that the molecules of water were particularly activated under the electromagnetic field in the MW oven, favouring the formation of the aldehyde **4** by oxidation of the alcohol promoted by the presence of Cr(III) centres. This behaviour could be profited from in further studies to synthesise fine chemicals in topotactic redox processes. Few examples, as for instance reactions taking place involving vanadium phosphates and arsenates,¹⁵ have been already reported. Additionally, the benzyl bromide gives 1,1'-[oxybis(methylene)]bisbenzene, **5**, as a derivative formed by condensation of the oxidised by-products.

It should also be mentioned that the yields of benzyl acetate and *n*-octyl acetate are notably reduced after "overheating" of the reaction mixtures, with a concomitant increase of the **5** by-product and *n*-octanol. This behaviour could be related to the stability of the resulting esters at these temperatures. In the case of benzoate, such consecutive reactions do not take place, probably due to the relatively higher stability of the benzoate esters. In comparing with anionic alkylations carried out using the solid supported phase procedure, it should be pointed out that the reaction of 1-bromooctane gave quite similar yields. Bram and co-workers¹ reported yields of 58% and 97% for the synthesis of C₆H₅CO₂C₈H₁₇ and CH₃CO₂C₈H₁₇, respectively, in reactions supported on alumina in dry media (20 h at 85 °C). As usually occurs in MW-assisted reactions using solid supports,^{3,5} we observe that the use of MW irradiation considerably reduces the reaction time in comparison with conventional heating at 100 °C. The temperatures reached in our experiments are always moderate, *i.e.* in the 120–150 °C range.

X-Ray diffraction patterns of the resulting powders showed that the 2D nature of the starting LDH matrix was preserved, although the interlamellar distances change after reaction (Fig. 1). For instance, the benzoate intercalation compound decreased from 1.52 nm to 0.78 nm after reaction with the benzyl bromide. This diminution was explained by the exchange of the benzoate anion by the bromide ion in the interlayer region of the solid during reaction. The carboxylate

Table 1 *O*-Alkylation yield (%) of LDH carboxylates reacting with *n*-octyl and benzyl bromides^a

1	+a		+b		1'	+a		+b	
	MW	Δ	MW	Δ		MW	Δ	MW	Δ
2	91.3	96	72.7	78.7	2'	78.1	82.5	53.5	69.7
3	4.1	—	7.3	7.6	3	17.5	7.2	18.4	19.6
4	—	—	7.1	—	4	—	—	13.1	—
5	—	—	12.9	12.9	5	—	—	13.5	10.7
Conversion	95.4	96	100	99.2	Conversion	95.6	89.7	98.5	100

^a MW: 600 W, 15 min; Δ: 100 °C, 5 h.

IR vibration bands of the unreacted solid in the 1800–1200 cm^{-1} region are replaced in the reacted solid (prior to solvent extraction) by low intensity bands at 1272 and 1700 cm^{-1} , which correspond to $\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}$ vibrations, indicating the formation of the ester in the selected example (Fig. 2).

Regarding the reaction mechanism, it should be pointed out that the low dipolar moment of the organic halides used, as well as the limited LDH swelling capacity, are factors that determine the controlled entry of these reagents into the inter-layer region of the solid where the active anions are located. We assume that this topotactic reaction takes place *via* diffusion of anions from the layer edges towards the intracrystalline space of the LDH solid, as proposed by Martin and Pinnavaia¹⁶ in the nucleophilic substitution reactions of halogen atoms of organic halides reacting with LDH exchanged by halides. In conclusion, although supported reactions between carboxylates and alkyl and aryl halides were previously studied,^{1,2} in the present work we report the reactivity of a solid material (an LDH) that contains carboxylates, selected here as a model example. According to the described general procedure, the nature of the anionic species (carboxylates in this case) involved in the reactions can be extended to other anions, in particular to unstable or toxic compounds in their anionic form. The processes reported here are topotactic reactions, which are completely different from the “conventional” procedures to activate anions on supported reagents such as alumina, but they give similar good yields. It will now be possible to conduct reactions involving anions in a constrained region, which could change the selectivity of the resulting products as reported for processes occurring in the interior of other layered or microporous solids.¹⁷ After reaction, it is possible to recover the solid, containing the other anion (bromide in our case) and, separately, the product of the reaction, the *O*-alkylated carboxylate compounds in these preliminary reported examples.

Further work is now in progress in order to investigate the influence of the nature of the cations located in the octahedral sheets of the LDH matrices, as well as the role of the water molecules in the studied reactions.

Experimental

The preparation of $[\text{Zn}_2\text{Cr}(\text{OH})_6]^+[\text{NO}_3^-] \cdot n\text{H}_2\text{O}$ was carried out as described in the literature.^{11–13} The intercalated LDH were obtained by anionic exchange: 1 g of ZnCr-NO_3 precursor was dispersed into a 1 M solution of the corresponding sodium carboxylate (acetate or benzoate). The reaction mixture was continuously stirred for 24 h at room temperature under a nitrogen flow. Then the precipitate was recovered by centrifugation and the resulting solid washed three times with deionized water and, finally, dried at room temperature.

These intercalation compounds were impregnated with a stoichiometric amount of halide, either 1-bromooctane or benzyl bromide, and placed in a Teflon[®] reactor. One

hundred milligrams of $\text{ZnCr-Ac} \cdot 3\text{H}_2\text{O}$ ($\text{ZnCr-Bn} \cdot 3\text{H}_2\text{O}$) were mixed with 29.9 μl (25.9 μl) of benzyl bromide or with 43.4 μl (37.6 μl) of 1-bromooctane. The reaction took place by heating either in a domestic MW oven (600 W power) or in a conventional oven at 100 °C. After the reaction was completed, the resulting products were extracted with methanol and analysed by GC-MS. The results of the alkylation of the intercalated carboxylates, after 15 min of MW treatment or 5 h of heating at 100 °C, are given in Table 1.

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