

Cyclodextrin-intercalated layered double hydroxides for fragrance release

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Abstract In order to attain the controlled release of fragrance, the intercalation of cyclodextrins (CDs) and fragrance in layered double hydroxides (LDHs) was examined. Carboxymethyl- β -CDs (CMCDs) of various degrees of substitution as well as Mg–Al support were synthesized. CMCDs were intercalated into LDH by the reconstruction method. Powder X-ray diffraction, thermal gravimetric analyses and Fourier transform infrared indicated a successful intercalation of CMCDs into the LDH gallery. The retention capacities of the hybrid materials were investigated in aqueous phase and in gaseous solution by static headspace gas chromatography and multiple headspace extraction. The functionalization of the LDH with CMCD allowed the encapsulation of various organic guests and could prolong the fragrance release time in comparison to that from LDH without CMCD, which can be attributed to the inclusion of the fragrance compound in the CMCD cavity.

Keywords Cyclodextrin · Layered double hydroxides · Intercalation · Fragrance · Static headspace · Controlled release

Abbreviations

β -CD	β -Cyclodextrin
CDs	Cyclodextrins
CMCD	Carboxymethyl- β -cyclodextrin
DS	Degree of substitution
FT-IR	Fourier transform infrared
LDH	Layered double hydroxides
MHE	Multiple headspace extraction
SHGC	Static headspace gas chromatography

Introduction

Layered double hydroxides (LDHs) are a class of anionic clays which can be represented by the general formula $[M_{1-x}^{II} M_x^{III}(\text{OH})_2]^{x+} [A^{n-}]_{x/n} \cdot y\text{H}_2\text{O}$ where M^{II} and M^{III} are di- and tri-valent metal cations respectively [1]. The positive charge of the layers is compensated by interlayer anions that can be exchanged for other inorganic or organic anions. This anion-exchange capacity offers LDHs a wide range of applications in areas such as catalysis [2, 3], pharmaceuticals [4], agriculture [5] or food additives [6]. The guest species however have of necessity to be anions for charge neutrality to be preserved, and as a consequence some guests are excluded. The intercalation of fragrances for instance has been little explored, owing to the difficulty of generating an anionic entity. However, when the interfacial surface of LDH is functionalized with anionic carboxymethyl- β -cyclodextrin (CMCD), it was found that the resulting hybrid material could retain a variety of organic compounds [7–9].

Cyclodextrins (CDs) are a family of cyclic oligosaccharides that are composed of α -1,4 linked glucopyranose subunit [10]. CDs have a low-polarity cavity in which

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organic compounds of appropriate shape and size can form inclusion complexes [11, 12].

Some researches regarding the uses of CDs in perfume and cosmetic industries have been reported [13–16]. Applications to cosmetics include solute stability, release control or malodor masking. The process of encapsulation is widely employed in the flavour industry to protect volatile and/or labile flavouring materials during storage. A variety of commercial practices are currently followed, but those involving the formation of flavour/CD molecular inclusion complexes afford some of the greatest potential for increased product shelf life. Although the intercalation of various CDs in LDH has been reported, few guests have been studied [7–9, 17, 18]. Except for iodine [18], all the guests were included from aqueous or ethanol solutions. Moreover, the release of the guests from the solid materials to the gaseous phase was never investigated. The research in this field area is relatively limited and, to the best of our knowledge, no study on the intercalation of fragrance materials into CDs functionalized LDH has been reported. A recent study on the intercalation of two fragrance compounds (vanillin and oil of wintergreen) in LDH showed that the controlled release of these compounds was little delayed by the simple intercalation inside LDH [5]. Thus, the use of CMCD–LDH could be a solution to provide a slower release of the fragrance compound. In this study we investigated the inclusion and the release of three volatile organic guests (two fragrances and toluene as a model compound) in aqueous phase and in gaseous phase.

Materials and methods

Chemical

β -Cyclodextrin (β -CD) was purchased from Wacker-Chemie (Lyon, France). $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, NaOH , Na_2CO_3 , bromoacetic acid, limonene, toluene and menthone (Aldrich), all of analytical reagent grade, were used as received. Distilled deionised water was used throughout this work.

Syntheses

Synthesis of CMCD

CMCDs with two degree of substitution (DS) were synthesized according to the procedure described in the literature [19] with some modifications. In brief β -CD (4.05 g) and NaOH (3.57 g) were dissolved in 20 mL of water and bromoacetic acid (3.47 g for DS = 4 and 6.94 g for DS = 7) was added with gentle stirring. The mixture was stirred for 1 h at ambient temperature. After pH

adjustment at 9, methanol was gradually added to the solution with stirring to obtain CMCD precipitation. The average number of carboxylated groups was calculated using ^1H NMR [20] and mass spectrometry after Sephadex G 10 purification.

Synthesis of LDHs

$\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)$ was prepared by coprecipitation by dropwise addition of known volumes of aqueous $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ into aqueous Na_2CO_3 and NaOH at a constant pH of 9.5, for 1 h at 63 °C according to the described procedure [21, 22]. The resulting slurry was heated at 60 °C for 24 h. Then, the precipitate was filtered, washed several times with hot deionized water (50 °C) to eliminate sodium ions and dried at 60 °C for 48 h.

Preparation of hybrid materials

The intercalation of CMCD within Mg–Al LDH was achieved using the reconstruction method, in which the LDH was calcinated at 500 °C during 5 h prior to ion exchange [23]. A solution of CMCD (500 mg) in deionised water was added to a suspension of LDH (2 g) in water, and stirred for 48 h at 60 °C under nitrogen atmosphere. pH was kept at 6. The white product was washed with water and dried for 12 h.

Inclusion of the guests within CMCD–LDH was performed in water solution during 24 h. In a typical inclusion experiment, 5 μL of a 10,000 ppm EtOH stock solution of the guest was allowed to equilibrate with a suspension of CMCD–LDH (50 mg) in water (10 mL) in a sealed vial and shake on a reciprocating shaker during 24 h.

The schematic illustration of the functionalization of the Mg–Al LDH by CMCD followed by inclusion of guest is presented on Fig. 1.

Characterization of the hybrid materials

Powder X-ray diffraction (XRD) analysis was performed on a Bruker Advance D8 powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Thermal gravimetric analyses (TGA) were realized with a Netzsch STA 409 apparatus. A sample mass of catalyst was loaded in an alumina crucible and heated from room temperature to 800 °C (heating rate: 5 °C min^{-1}) in air flow (75 mL min^{-1}). Fourier transform infrared (FT-IR) absorption spectra were recorded using the KBr pellet technique on a FT-IR Equinox 55 Bruker spectrometer in the range 4,000–400 cm^{-1} and a resolution of 4 cm^{-1} . BET surface areas of the solids were measured by nitrogen adsorption at –196 °C using a Surface Area Analyzer 2010, ASAP apparatus. The samples were outgassed for 1 h at 120 °C.

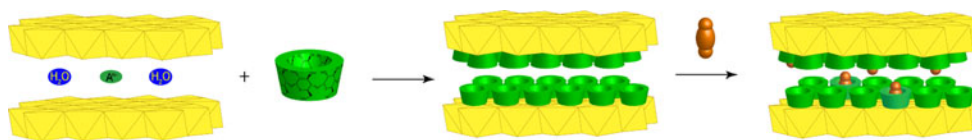


Fig. 1 Schematic illustration of the functionalization of LDH by ion exchange with CMCD followed by inclusion of guests

Static headspace gas chromatography

Headspace sampling is employed with gas chromatography (GC) in numerous fields and with a variety of applications [24, 25]. A headspace sample is in principle a gas sample which has been previously in contact with a liquid or solid sample from which volatile compounds were released into the gas with subsequent analysis by GC. Headspace GC is therefore a technique of gas extraction and can be carried out comparable to a solvent extraction as a one-step extraction (static or equilibrium headspace) or as a continuous extraction (dynamic headspace) [26].

Measurements were conducted with an Agilent headspace autosampler under solid support or aqueous media. The oven-dried materials were weighed in glass vials of 20 mL in volume. For studies under aqueous media 10 mL of distilled deionised water were added in the vial. After addition of the sorbate with a microsyringe, the vial was sealed using silicone septa and aluminium foil. The vials were then thermostated at 25 ± 0.1 °C. After the equilibrium was established (24 h), 1 mL of vapor from the above solution was drawn out from the vial using a gas-tight syringe and injected directly in the chromatographic column via a transfer line.

This sample was then analyzed by GC (Perkin Elmer Autosystem XL) equipped with a flame-ionization detector using an Agilent J&W DB-624 column. The obtained chromatograms allow quantitative analysis of the vapor above each sample. Blank experiments (without sorbents) were used to account for sorption losses.

Formation constant determination

The host/guest system was studied by a static headspace gas chromatography (SHGC) titration method developed in our laboratory for volatile organic compounds [14, 27–29]. Different concentrations of CD were used at constant guest (G) concentration. An algorithmic treatment was then applied to minimize the difference between the experimental and theoretical values of the peak area leading to the adequate formation constant (K_f) [30].

Retention of organic compounds by hybrid materials

The percentage of retention (r) of the studied aroma by the different adsorbent is expressed as follows:

$$r(\%) = (1 - A_{\text{Ads}}/A_0) \quad (1)$$

with A_0 and A_{Ads} the peak area of the aroma in the absence and in the presence of adsorbent respectively. The percentage of retention was determined at 25 °C for a 10 ppm solution of the aroma and a weight of 50 mg for CMCD, LDH and CMCD–LDH. For each adsorbent, measurements were done in triplicate.

Multiple headspace extraction (MHE)

In order to study the dynamic release of aroma from CMCD–LDH we used MHE. In principle, MHE is a dynamic gas extraction carried out stepwise. If we take successive aliquots from the vial's headspace, the total amount of the analyte present will further decline, eventually becoming totally exhausted. In each step, part of the analyte present is removed until no analyte is left in the original sample. Thus, the sum of the amounts of the analyte removed in the individual extractions will be equal to the total amount of analyte present in the original sample [26].

One hundred milligrams of the hybrid material containing the guest were placed in a sealed vial at 60 °C. Fifty successive extractions were realized.

Results and discussion

Characterization

Powder XRD

The powder XRD patterns of LDH and CMCD–LDH are presented in Fig. 2. As compared to the Mg-Al-CO_3^{2-} (Fig. 2a, $2\theta = 11.2^\circ$, $d_{003} = 0.78$ nm), the basal reflection (003) of both CMCD–LDH shifts to a lower 2θ angle. This may indicate the intercalation of CMCD into galleries of LDH.

Thermal gravimetric analyses

TGAs of CMCD and CMCD–LDH (Fig. 3) show a two-steps weight loss. The first was attributed to the loss of water and interlayer water molecules and the second to the dehydroxylation and elimination of anions. In the cases of

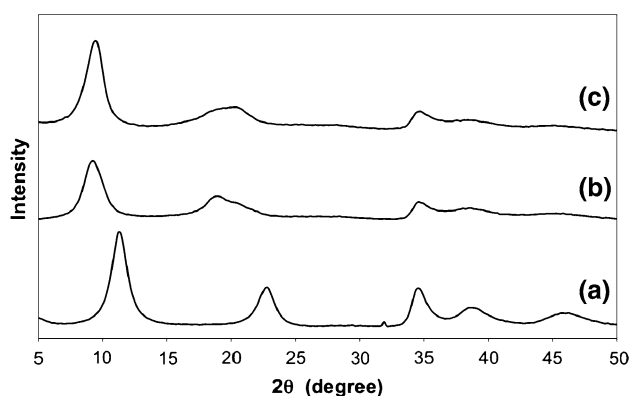


Fig. 2 XRD patterns of (a) Mg–Al LDH, (b) CMCD 4–LDH and (c) CMCD 7–LDH

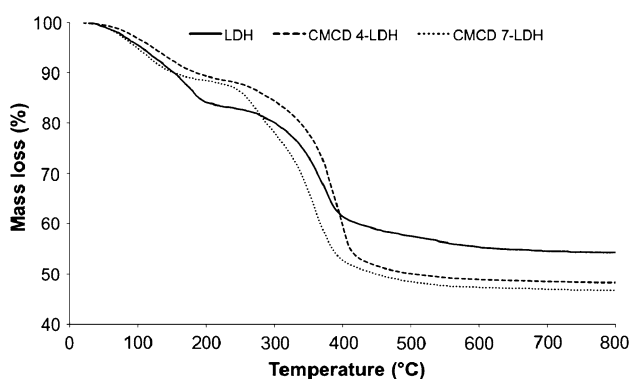


Fig. 3 TGA curves for Mg–Al LDH, CMCD 4–LDH and CMCD 7–LDH

CMCD–LDH, the second weight loss was attributed to the simultaneous decomposition of CMCD together with the breakdown of the LDH structure [17]. From these weight losses, the amount of CMCD 4 and CMCD 7 in the hybrid material was calculated to be 94 and 83 mmol/kg LDH respectively.

Infrared spectroscopy

The FT-IR spectra of CMCD and CMCD–LDH are presented in Fig. 4, and the peak position and their assignments are given in Table 1. As may be seen from Fig. 2, the position of most bands shows no change on intercalation. The modified bands are the C–O stretch of the carboxylate group that appears at $1,603\text{ cm}^{-1}$ in the CMCD sodium salt and at $1,594\text{ cm}^{-1}$ in the CMCD–LDH, and the bands associate with the $-\text{CH}_2\text{OH}$ group ($580\text{--}800\text{ cm}^{-1}$). These data are in good agreements with data from Mohanambe and Vasudevan [31] and Zhao and Vance [32] and clearly demonstrate that CMCD had been adsorbed by LDH.

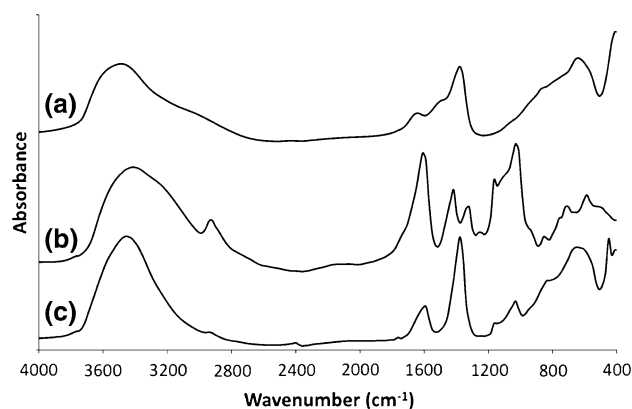


Fig. 4 Infrared spectra of (a) Mg–Al LDH, (b) CMCD 7 and (c) CMCD 7–LDH

Table 1 Infrared assignments of CMCD and CMCD–LDH

CMCD (cm^{-1})	CMCD–LDH (cm^{-1})	Assignments
3407	3447	O–H stretch
2930	2934	C–H stretch
1603	1594	C–O stretch of $-\text{COO}$
1420	1382	O–C–H, C–C–H, C–O–H bending
1160, 1029	1162, 1031	C–O stretch
949	948	C–C stretch
757, 709, 608, 579	796, 762, 615, 581	Internal rotation modes about $-\text{CH}_2\text{OH}$
–	447, 659	M–OH stretch

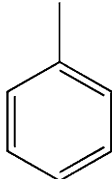
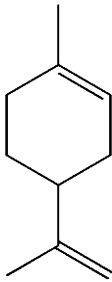
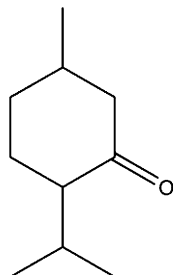
Table 2 Specific surface area (m^2/g) of LDH and CMCD–LDH

Sample	Specific area (m^2/g)
Native LDH	62 ± 2
Calcinated LDH	150 ± 2
CMCD 4–LDH	5 ± 1
CMCD 7–LDH	19 ± 2

Specific surface area

Table 2 shows specific areas values of the LDH materials uncalcined, calcined at 500 °C and functionalized with CMCDs. The specific area values for uncalcinated and calcinated LDH are in good agreements with the values observed in literature for the same LDH (71 and $91\text{ m}^2/\text{g}$ respectively) [33]. The calcination of the LDH leads to an increased surface area. After intercalation of CMCD, the surface area decreases. These results prompted us not to increase the CD content of the hybrid material, even if higher contents have been used in literature [17].

Table 3 Structure and formation constants (M^{-1}) of the studied guest with CMCDs (standard deviation values are <10 %)

Guest	Structure	β -CD	CMCD 4	CMCD 7
Toluene		142 ^a	122	83
Limonene		3457 ^b	2078	1081
Menthone		656	621	283

^a From Ref. [28]^b From Ref. [14]

Formation constant determination

The determinations of the formation constant between CMCDs and guests were done at 25 °C using four CDs concentrations. The obtained variations of the peak area are in good agreements with a 1:1 host/guest complex. The formation constants calculated with the algorithmic treatment are reported in Table 3 in comparison with values obtained for β -CD. As one can see in Table 3, if the substitution of β -CDs hydroxyls by carboxymethyl groups leads to slightly lower formation constants towards the studied guests, inclusion ability remains.

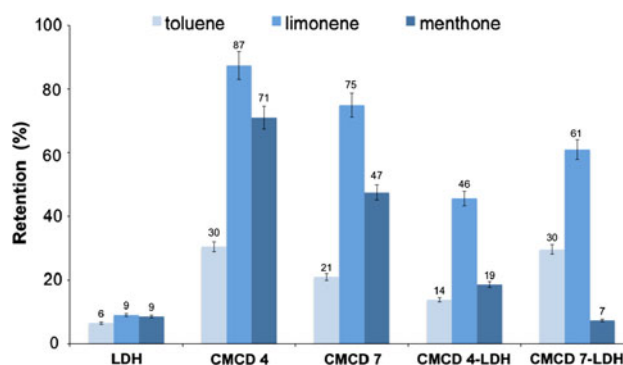
Retention of guest by CMCD–LDH

The presence of chemical agents in solution is known to impact the vapor–liquid equilibria since they can change the solubility of hydrophobic compounds, for example, by forming inclusion complexes as in the case of CDs [34, 35].

The presence of LDH, CMCD or CMCD–LDH modified the vapor–liquid equilibria for all the studied compounds,

which were all more retained in aqueous solution in presence of the different adsorbent. The results obtained in aqueous media are presented in Fig. 5.

As can be seen from Fig. 5, LDH have a poor retention capacity (<10 %) for the three guests. CMCDs retain the guests in the following order limonene > menthone > toluene. These results are correlated with the experimental

**Fig. 5** Retention of the guests by the different supports in aqueous solution

stability constants. For instance, the trapping ability of CMCD 7 is lower than CMCD 4. CMCD 7-LDH presents higher efficiency than CMCD 4-LDH except for menthone. The retention capacities of CMCD-LDH are lower than CMCD alone. However, if we consider that hybrid materials contain less CD cavity, their efficiency is higher than CMCD alone. Moreover hybrid materials are insoluble in water and can be used for organic compounds recovery from aqueous solution.

In the case of limonene, we also investigated the retention capacities of the hybrid materials in gaseous phase. In this case, 50 mg of solid support is exposed to 5 μ L of limonene in a sealed vial. The retention capacities of CMCD 4-LDH and CMCD 7-LDH are close to the values in aqueous phase (43 and 63 % respectively). No retention was observed for CMCD alone and only 10 % for LDH. These results confirm the data observed by Mahanambe and Vasudevan [18] with exposure of CMCD-LDH to iodine vapor: appropriate functionalized LDH can adsorb guest from gaseous phase but this is not the case for LDH alone.

Although the amount of CMCD 4 and CMCD 7 in the hybrid material was quite similar (94 and 83 mmol/kg respectively), the specific surface area of CMCD 7-LDH is four time bigger than the specific surface area of CMCD 4-LDH. This difference in surface area could be due to the fact that some CMCD molecules could be intercalated in the gallery of LDHs and another part adsorbed on the surface of LDHs. The efficiency of the CMCD-LDH materials depends both on the specific surface area and on the formation constant of the guest with the CMCDs, thus explaining some retention differences between the hybrid materials and the CD hosts.

Multiple headspace extraction (MHE)

The same amount of limonene is placed in a seal vial with solid support and without solid support (blank experiment). The amount of limonene present in the vial after each extraction is determined using the peak area. The sum of the amounts of limonene removed in the individual extractions will be equal to the total amount of limonene present in the original sample. Thus the retention of the solid support can be evaluated and compared to the blank experiment. The retention percentages obtained for each successive extraction are presented in Fig. 6.

The results obtained in MHE extraction are correlated with the retention obtained in static experiments. While the release profile with LDH is comparable to the blank experiment, both CMCD-LDH hybrid materials retain limonene with a good efficiency. This means that the release of such compounds could be effective for a long period in the presence of such adsorbent.

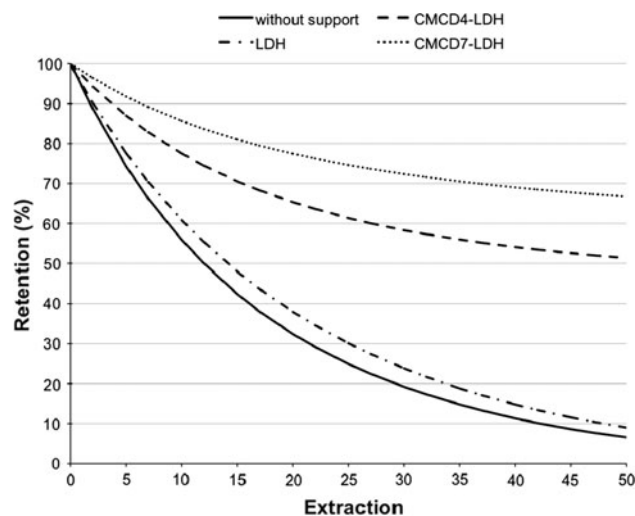


Fig. 6 MHE of limonene in gaseous phase in absence of support and in presence of LDH and CMCD-LDH

Conclusion

Two CMCDs have been intercalated in Mg–Al LDH followed by the inclusion of volatile organic compounds. MHE was used to investigate the release of fragrance compounds from LDH. It was found that the use of CMCD-LDH allows the controlled release of aroma compounds. The potential applications of these hybrid materials are considerable and include the manufacture of air fresheners with enhanced flavor retention, adsorbent for organic pollutants or controlled delivery of drugs.

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