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4-Benzoylbenzoate intercalated in layered double hydroxides: a new catalyst for photo-oxidation of sulfides in solution and in the gas phase

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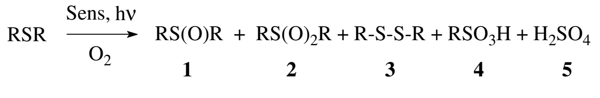
Abstract—A new mixed organic–inorganic photosensitizer, based on 4-benzoylbenzoate intercalated into a layered double hydroxide has been prepared, characterized and successfully tested for the photo-oxidation of dialkylsulfides, both in acetonitrile and in the gas phase.

Photo-oxidation of sulfides is a well documented and extensively studied reaction.[1] At short wavelength, the reaction is achieved through photolysis[2] or, at longer wavelengths, sensitized with singlet oxygen[3,4] or electron transfer photosensitizers.[5,6] In the latter case, benzophenone derivatives (either soluble or grafted on silica) already proved to be efficient photocatalysts, both in water and in acetonitrile solutions.[5,7] Grafted silicas have several advantages like easier separation from reaction products and reusability. However, chemical grafting presents some disadvantages: multistep synthesis has to be performed and the amount of grafted benzophenone remains low ($0.5\,\mathrm{mmol\,g^{-1}}$). Due to the weak molar absorption coefficient of benzophenone at 350 nm ($\varepsilon = 240\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), large amounts of silica grafted photosensitizers are needed to achieve high photooxidation yields.

Silica is not the only inorganic matrix used in the field of supported photosensitizers. For example, polyoxometallate[8] or pthalocyanines[9] supported photosensitizers have been prepared by their intercalation in lamellar materials like Mg–Al layered double hydroxides (MgAl-LDH). However, the use of intercalated organic photosensitizers has been rather seldom described.[10] For example, irradiation of a clay co-adsorbed mixture of *trans*-cinnamate and 4-benzoyl benzoate ions in suspension resulted in efficient formation of a *syn* head-to-head dimer. The synthesis of the material involved anion exchange or reconstruction from commercial LDH, without any detailed characterization of the intercalation or adsorption.[11,12]

Generally speaking, numerous examples of insertion of organic hosts in LDH are described in the recent literature,[13] and the field of applications of such hybrid organic–inorganic materials is still growing: catalysis of organic reaction,[14] adsorption of organic and inorganic pollutants,[15] controlled release of pharmaceutically active compounds.[16] In the field of catalytic oxidation, sulfides were efficiently converted to sulfones by an osmate molecular oxygen system immobilized on MgAl-LDH, recently developed by Choudary et al.[17]

We report here the preparation and characterization of a benzophenone derivative, 4-benzoylbenzoate (4-BB) intercalated in a MgAl-LDH by direct synthesis. This material is used for the first time for the photo-oxidation of di *n*-butylsulfide (DBS) in acetonitrile solution (Scheme 1). Its photo-oxidizing ability towards gaseous dimethyl sulfide (DMS) has also been studied at the gas-solid interface.



$$\mathrm{RSR} \xrightarrow[\mathrm{O_2}]{\text{Sens, h}\nu} \underset{\mathbf{1}}{\mathrm{RS(O)R}} + \underset{\mathbf{2}}{\mathrm{RS(O)_2R}} + \underset{\mathbf{3}}{\mathrm{R\text{-}S\text{-}S\text{-}R}} + \underset{\mathbf{4}}{\mathrm{RSO_3H}} + \underset{\mathbf{5}}{\mathrm{H_2SO_4}}$$

Scheme 1. Photo-oxidation of di *n*-butylsulfide in acetonitrile.

Keywords: 4-Benzoylbenzoate; Layered double hydroxide; Photooxidation; Sulfide.

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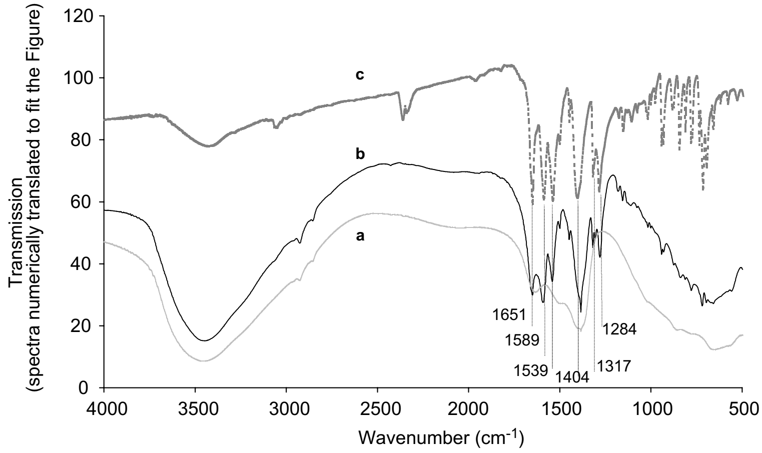

Figure 1. FTIR spectra of: (a) nonintecalated LDH (HT0), (b) 4-BB/HT1, (c) pure 4-BB.

The materials 4-BB/HT1 and 4-BB/HT2, which differ by the Mg/Al ratio, are prepared by direct synthesis at controlled pH[†]. Microanalyses are consistent with extensive incorporation of the organic anion. The amount of intercalated 4-BB does not differ significantly between the two materials (1.91 and $1.81\,\mathrm{mmol\,g^{-1}}$)[18] despite the different Mg/Al ratio. In the following, all the results are presented on 4-BB/HT1, as the other material gives comparable spectra.

Nitrate anions are still present in the material as confirmed by the band at $1400\,\mathrm{cm^{-1}}$ in the FTIR spectra in KBr pellets (Fig. 1). Neither significant shift nor new signals are observed relative to the spectra of pure 4-BB, indicating that 4-BB is not grafted into the clay but only intercalated. Direct evidence for intercalation is obtained from XRD analysis. The parent LDH sample exhibits an XRD pattern (Fig. 2a), characteristic of a well-crystallized layered structure of hydrotalcite-like type (JCPDS file No. 37-0630)[‡]. The *d* spacing calculated is 7.70 Å ((0 0 3) line). The height of the interlayer is estimated to be ca. 2.9 Å as previously referred by Miyata[19] and the thickness of the brucite-like octahedral hydroxide layer made with Mg and Al is 4.78 Å from the interlayer distance. The *c* (basal spacing) and *a* lattice parameters (determined by least squares refinement) are, respectively, 23.12 and 3.02 Å. The XRD pattern of 4-BB/HT1 (Fig. 2b) highlights the structural changes following the insertion. It clearly indicates the presence of a new phase (associated with 4-BB intercalated in the interlayer region) together with the hydroxyl phase.

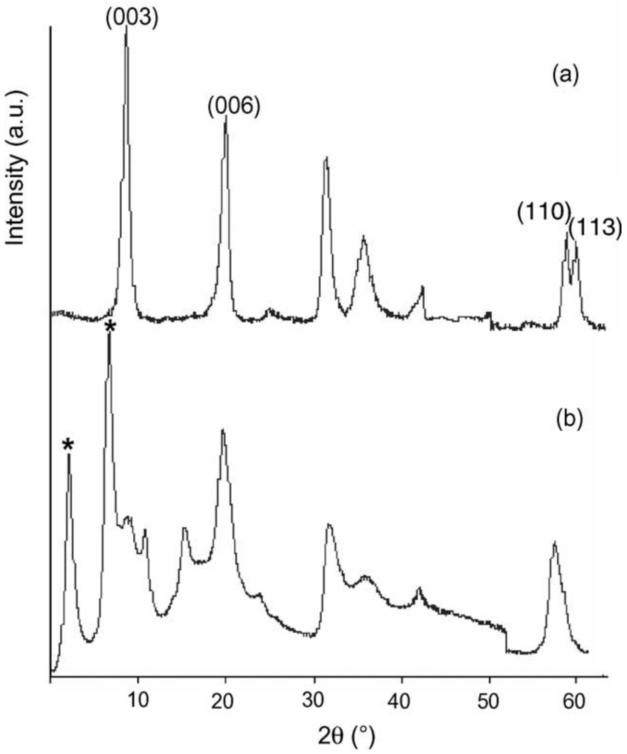

Figure 2. X-Ray diffraction pattern of (a) nonintercalated LDH (HT0), (b) 4-BB/HT1.

Relative to the parent LDH pattern, the presence of supplementary reflections (indexed by an asterisk on Fig. 2) is noted. The (0 0 3) and (0 0 6) reflections are shifted to the smaller angles, as previously reported for some other hybrid structures.[20,21] This reveals an enlargement of the basal spacing corresponding to an expansion of the interlayer space to about 15.1 Å. Note that simultaneously, an increase of the structural disorder was observed. The symmetric (1 1 0) and (1 1 3) reflection merged, possibly indicating a disturbance of the brucite-like layer structure. The coexistence of the pure Mg–Al hydrotalcite phase reflections with the hybrid phase reflections on the same pattern indicates an

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[†] 100 mL of a water (treated by inverse osmosis) solution of $Mg(NO_3)_2$, $6H_2O$ and $Al(NO_3)_3$, $9H_2O$ ($0.1\,\mathrm{mol\,L^{-1}}$) in a Mg/Al ratio of 2 (4-BB/HT1) or 2.5 (4-BB/HT2) and 100 mL of a 4-BB ($0.11\,\mathrm{mol\,L^{-1}}$) and NaOH ($2\,\mathrm{mol\,L^{-1}}$) solution are added dropwise while carefully controlling the pH between 8 and 10. The slurry is stirred for 12 h at 60 °C, then filtered and washed thoroughly with hot water. The filter cake is then dried at 353 K for 15 h.

[‡] JCPDS files numbers are from the Mineral Powder Diffraction Data Files Library, International Center for Diffraction Data, Swarthmore, PA, USA.

inhomogeneous insertion of 4-BB in the host structure, and, probably, remaining nonintercalated zones.

Photo-oxidation experiments are performed both in solution and in the gas phase. In the first case, 10 mL of 1.15×10^{-2} mol L^{-1} di *n*-dibutylsulfide (DBS) acetonitrile solutions containing 30 mg of the solid photocatalyst and cyclododecane as internal standard in a Pyrex reactor are used. The stirred slurry is continuously bubbled with pure oxygen and irradiated with four fluorescent 350 nm lamps in a RAYONET® device. After filtration, the composition of the irradiated solution is determined by GC-FID for volatile compounds, by ion exchange chromatography for acidic species and by UV spectrometry in order to check the possible presence of 4-BB in solution.

In the second case, preliminary attempts were performed with a fluidized bed of 4-BB/HT1 in a 20 mL Pyrex vertical reactor (500 mg of 4-BB/HT1). The gaseous effluent (100 ppmv of dimethylsulfide (DMS)) is continuously introduced at a constant flow (250 mL/mn). The gas flow at the outlet of the reactor is analyzed each seven minutes with a GC-FID chromatograph with an automatic injection loop.

In acetonitrile solution, blank experiments without sulfide indicate that the lamellar structure is preserved under irradiation in the presence of oxygen and that less than 1% of 4-BB is released in the solution. We first verified that with this amount of 4-BB in solution, no oxidation of sulfide occurred under homogeneous conditions. Second, we checked that DBS did not react when HT0 (without 4-BB) was used. Comparative photooxidation experiments were then performed with 30 mg of the intercalated materials (corresponding to a known amount of 4-BB deduced from the microanalysis data) or with equivalent amounts of 4-benzoyl benzoic acid (4-BBac) in homogeneous solution (Table 1). Three main conclusions may be drawn from this table.

(1) First, the intercalated material reacts more sluggishly than soluble 4-BBAc, since after 1 h irradiation, 30% of the sulfide is not converted. This probably results from the hindered diffusion of the reactants inside the lamellar structure in the heterogeneous case, as already reported with phthalocyanines intercalated in LDH.[9]
(2) Second, although the XRD pattern of the irradiated 4-BB/HT1 is still characteristic of a preserved LDH structure, some 4-BB is found in acetonitrile (5%) contrary to the blank experiments. This exchange is closely related to the initial concentration of sulfide, since with more concentrated DBS solutions (10^{-1} mol L^{-1}), greater amounts of 4-BB are released in solution (42%) upon irradiation. This can be accounted for by surface exchange between 4-BB and formed sulfate and sulfonate as suggested by the XPS analysis of the irradiated 4-BB/HT1.
(3) Third, 4-BB/HT1 appears much more selective towards sulfoxide formation and only minor amounts of disulfide, sulfone and acidic compounds are obtained. In both homogeneous and heterogeneous case, it may be noticed that sulfone is mainly observed at long irradiation time. It is known from previous studies that disulfides and acids arise, respectively, from the dimerization or from the oxidation by ground state oxygen of thiyl radicals.[2] Moreover, it has been shown that under benzophenone sensitization, both electron transfer (with formation of an ion-pair $RSR^{\cdot+}$, $O^{\cdot-}$) and singlet oxygen addition to sulfides are competitive.[7] Our results thus strongly suggest that the electron transfer mechanism, which is only able to lead to acidic products, is less favored with the lamellar material. This may be tentatively accounted for by the unfavorable formation of charged $RSR^{\cdot+}$ between the positive brucite sheets.

Finally we examined the turnover of 4-BB/HT1 for sulfide oxidation. In these experiments, a slurry of the photocatalyst was irradiated for 150 min. The clay was then removed by filtration, and the filtrate analyzed. After washing with acetonitrile, the clay was then reused in successive trials. Table 1 shows that 4-BB/HT1 is active during at least three consecutive runs and that sulfoxide is always the major product. The formation of sulfone decreases from the first to the third trial. The absence of other by-products and the stability of the amount of 4-BB found in solution after irradiation (5%) are also noteworthy. After the last run, the catalyst is removed by filtration. After evaporation of acetonitrile, the crude product is diluted in a chloroform solution, washed with a carbonate aqueous solution to take off the released 4-BB, and purified on a silicagel column. The yield in isolated sulfoxide is 80% (eluent chloroform).

Some experiments have been attempted towards the gas phase photo-oxidation of dimethylsulfide (DMS) with

Table 1. Composition of the solutions after irradiation

	Time (h)	**1**[b]	**2**[b]	**3**[b]	**4**[b]	**5**[b]	4-BB released[c]
4-BBAc	1[a]	58	2	12	5	0.5	—
4-BB/HT1	2[a]	76	1	1	1	0.1	4
4-BB/HT1 (cycle 1)	2.5	74	10	0	Nd[d]	Nd[d]	5
4-BB/HT1 (cycle 2)	2.5	81	6	0	Nd[d]	Nd[d]	5
4-BB/HT1 (cycle 3)	2.5	88	5	0	Nd[d]	Nd[d]	5

[a] Time for total consumption of sulfide.
[b] % Relative to the initial sulfide concentration.
[c] % Released in solution relative to the initial amount of inserted 4-BB.
[d] Not determined.

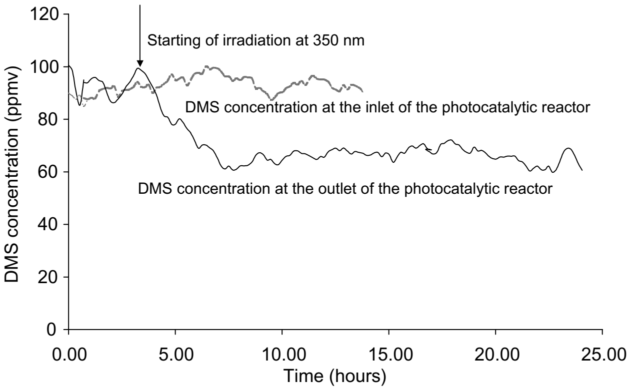

Figure 3. Evolution of dimethylsulfide concentration in the gas phase outside the reactor and through the reactor under irradiation.

the same material. In the absence of irradiation, the DMS concentration in the gas phase is the same when the effluent flows outside or through the reactor even in the first chromatographic runs: this means that no significant adsorption of DMS occurs on the modified LDH. Irradiation of the reactor at 350 nm with 12 fluorescent lamps lowers the concentration of DMS by about 30%, with simultaneous observation of dimethylsulfoxide. Under these experimental conditions, the photoactivity of 4-BB/HT1 holds on for more than one day without any decrease (Fig. 3).

This result implies that 4-BB/HT1 can achieve the partial photo-oxidation of DMS at the gas–solid interface.

In summary, intercalation of 4-BB inside an LDH material has been achieved, with a noticeable increase of the interlamellar distance. This material proved to be an efficient and reusable oxidation photocatalyst in solution. The enhanced selectivity of the material towards sulfoxide can be attributed to unfavourable electrostatic effects. In the gas phase, optimization of the adsorption of the sulfide on the material and of the contact time have to be sought in order to improve the DMS photo-oxidation yield.

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18. 4-BB/HT1:Mg/Al = 2, %C, expt (theor): 31.88 (32.01); %H, expt (theor): 4.49 (4.54); Formula: $[Mg_{0.67}Al_{0.33}(OH)_2]$4-$BB_{0.27}^{-}(NO_3)_{0.06}^{-}$,$H_2O$ 4-BB/HT2:Mg/Al = 2.5, %C, expt (theor): 29.72 (29.10); %H, expt (theor): 4.49 (4.34); Formula: $[Mg_{0.71}Al_{0.29}(OH)_2]$-4-$BB_{0.23}^{-}(NO_3)_{0.06}^{-}$, $0.7H_2O$.
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