Photocatalytic oxidation of aliphatic and aromatic sulfides in the presence of silica adsorbed or zeolite-encapsulated 2,4,6-triphenyl(thia)pyrylium

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Abstract

Solid photocatalysts in which the 2,4,6-triphenylpyrylium (TP) or 2,4,6-triphenylthiapyrylium cation (TTP) are encapsulated within zeolite Y or deposited on mesoporous silica are used as photosensitizers for the oxidation of sulfides, both aromatic and aliphatic, in solvents of various polarity. Contrary to the same cations in solution, these solid sensitizers are not significantly degraded during operation. An effective oxygenation takes place leading to sulfoxides, disulfides, sulfinic and sulfenic esters as well as sulfonic acids. This large scope method shows a limited dependence on the substrate structure and on conditions and is suitable for the abatement of sulfur-containing pollutants.
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1. Introduction

Photosensitized oxygenation is a typical 'advanced oxidation method', characterized by the environmentally friendly conditions [1]. The key step in such reactions, activation of oxygen, occurs according to different mechanisms, typically involving singlet oxygen, superoxide anion or hydroxyl radicals [2]. A main problem in every case is that the sensitizers themselves are liable to the action of such reactive oxygen species and are consumed at a rate comparable to that of the substrates. Therefore one loses one of the key advantages of a photosensitized process, that is that only a minimal amount of a chemical, the sensitizer, has to be added. This limitation does not apply to inorganic materials, in particular to largely used semiconductor oxides [3–5]. An alternative choice is protecting the organic sensitizers by immobilizing in the cavities of a solid support [6–17]. This arrangement combines the better control

of the reaction typical of organic sensitizer with the robust nature of heterogeneous photocatalyst.

The purpose of this work is twofold, on one hand testing the efficiency and the stability of some immobilized photocatalysts based on the (thia)pyrylium cation in oxidation processes even when operating on a relatively large amount of substrates and on the other one assessing the usefulness of such materials in an application of practical significance, that is the oxidation of sulfides. This is a process of interest in various fields, from synthetic chemistry (oxidation to sulfoxides reverts the electronic character of the sulfide moiety and introduces a stereocenter) to the modeling of biochemical oxidations. From the environmental point of view, serious problems are the desulfurization of fossil fuels [18], the removal of foul smelling sulfides from exhaust of various nature, from meat rendering plants [19] to industrial wastewater treatment plants [20] and the disposal of sulfur-containing chemical warfare agents [21].
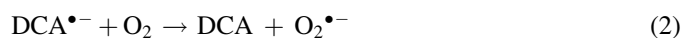
Oxidative desulfurization by various reagents has been studied extensively in recent years for such applications [22–25]. As an example, a high conversion of sulfides to sulfones and sulfoxides provides a difference in polarity that

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can be used for the selective removal of such substances with solid adsorbents, in order to obtain fuel that meets the increasingly stringent purity standards and avoid damage to catalytic converters [26].

Although effective procedures have been reported, some limitations remain and at any rate the ideal method should use directly oxygen, rather than introducing a potentially polluting reactant such as a strongly oxidizing chemical agent, and be characterized by mild conditions and general application. Photochemistry may be a sensible choice, in particular if a photosensitized method is used that is effective under solar light. The extensively investigated dye-sensitized ('Type II') oxidation via singlet oxygen [2,27,28] satisfies this require-ment, but is effective only with aliphatic sulfides in protic solvents [29–31] (while, e.g. for desulfurization of fuels aromatic sulfides are even more important than the aliphatic ones and the medium is nonpolar). Titanium dioxide has been used in solution for (hetero)aromatic sulfides [32] and in the gas phase for aliphatic derivatives, where deactivation of the photocatalyst occurred, however [33]. The use of different organic photosensitizers may enlarge the scope of the reaction. Thus, with an electron-withdrawing substituted aromatic, e.g. 9,10-dicyanoanthracene (DCA), oxidation of aromatic sulfides was obtained via an alternative path, that is an electron transfer (ET) and generation of superoxide (Eqs. (1)–(3)) [34–37].

$$^1DCA + RR'S \rightarrow DCA^{\bullet-} + RR'S^{\bullet+} \tag{1}$$

$$DCA^{\bullet-} + O_2 \rightarrow DCA + O_2^{\bullet-} \tag{2}$$

$$RR'S^{\bullet+} + O_2^{\bullet-} \rightarrow RR'SO \tag{3}$$

In order that this mechanism operates, the sulfide concentration must be sufficiently high as to effectively quench the short-lived singlet excited DCA (Eq. (1)), since spontaneous intersystem crossing (ISC) to the long-lived triplet is inefficient. At high sulfide concentration, quenching of the singlet yield ^3DCA and thus an efficient oxidation (quantum yield up to 2) may take place, but this may be a limitation when a low concentration of sulfides is used [36,38]. Ideally, a general method should be able both to degrade a large amount of the pollutant and to reach a very low residual concentration. For this aim pyrylium salts (P^+) are better suited, since they are characterized by a rather efficient ISC, and not only the singlet (τ_S 2.9 ns) but also the triplet (τ_T ca. 10 μs) can operate as an oxidant [39,40]. With adamantyleneadamantane these sensitizers have been demon-strated to induce ET either to the singlet or to the triplet according to the substrate concentration [39]. Both states are good enough oxidants for accepting an electron from sulfides (see Eqs. (4) and (5)).

$$^1P^+ + RR'S \rightarrow P^{\bullet} + RR'S^{\bullet+} \tag{4}$$

$$^3P^+ + RR'S \rightarrow P^{\bullet} + RR'S^{\bullet+} \tag{5}$$
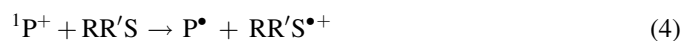
Indeed, pyrylium salts absorb blue light and cause sulfoxidation with reasonable efficiency (with both aromatic and aliphatic sulfides), although the mechanism has not yet clearly deter-mined because, differently from the $DCA^{\bullet-}$ case, reduction of

oxygen by $P^{\bullet}$ is ineffective [35,36]. Possibilities that have been considered are a reaction of the sulfide radical cation directly with oxygen (Eq. (6)) and the formation of some oxygen adduct from $P^{\bullet}$, which then is the active species in the oxidation (Eqs. (7) and (8)).

$$RR'S^{\bullet+} + O_2 \rightarrow RR'SO \tag{6}$$

$$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet} \tag{7}$$

$$PO_2^{\bullet} + RR'S \rightarrow RR'SO \tag{8}$$

Apart from mechanistic problems, the limitation to the practical application of P^+ for sulfoxidation is that such materials are photolabile, a common shortcoming with organic sensitizers, as mentioned above, which is even more important in this case. One of the ways for overcoming this limitation is incorporating the sensitizer into a solid phase, as indeed has been done for other photosensitizers of various classes, both by covalent bonding and by different complexation and trapping. Pyrylium salts trapped in zeolites have been first tested by some of the present authors, mainly with thianthrene with a starting con-centration around 100 ppm [15,16]. Developing this hint, we carried out a comprehensive study of the photooxidation of aliphatic and aromatic sulfides by using some solid phase incorporated pyrylium salts, higher starting concentrations and in different solvents.

2. Experimental

2.1. Preparation and characterization of the photocatalysts

SiO$_2$ (Basf, 200 m^2 g^{-1}) and the zeolite HY (PQ CBV 720) were commercial samples. MCM-41 (Si/Al 13) was synthe-sized according to a known experimental procedure by using cetyltrimethylammonium bromide and an aerosil and alumina as silicon and aluminum source, respectively [41,42]. The crystallinity of MCM-41 samples was determined by powder X-ray diffraction. The surface area was measured by isothermal N$_2$ adsorption using a Micrometrics 2000 ASAP apparatus.

The tetrafluoroborate of 2,4,6-triphenylpyrylium (TPT) was supplied by Aldrich and the thia analogue TTP perchlorate was synthesized by reacting TP$^+$ with SH$^-$ as reported in the literature [43,44]. TP$^+$ on silica and TP$^+$ on MCM-41 were prepared by depositing from a dichloromethane solution given amounts (4% loading) of TP$^+$ onto thermally dehydrated (120 °C, 2 h) silica or MCM-41.

TPT–HY was prepared starting from commercial HY by following the reported procedure [16]. For preparing TTPT–HY a solution of chalcone (21 mg) and acetophenone (12 mg) in cyclohexane (10 mL) saturated of H$_2$S was magnetically stirred in the presence of thermally dehydrated (500 °C) HY at reflux temperature for 3 days while a constant stream of H$_2$S was flowed through the system according to the method reported in the literature [6]. During the ship-in-the-bottle synthesis the solid became increasingly orange in color. After this time, the raw solid photocatalyst was submitted to