



Selective oxidation with nanoporous silica supported sensitizers: An environment friendly process using air and visible light

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ABSTRACT

Transparent and porous silica xerogels containing various grafted photosensitizers (PSs) such as anthraquinone derivatives, Neutral Red, Acridine Yellow and a laboratory-made dicyano aromatics (DBTP) were prepared. In most cases, the xerogels were shown to be mainly microporous by porosimetry. The PSs were characterized in the powdered monoliths (form, aggregation, concentration) by electronic spectroscopy which also proved to be a useful tool for monitoring the material evolution after irradiation. These nanoporous xerogels were used as microreactors for gas/solid *solvent-free* photo-oxygenation of dimethylsulfide (DMS) using visible light and air as the sole reactant. All these PSs containing monoliths were efficient for gas–solid DMS oxidation, leading to sulfoxide and sulfone in varying ratios. As these polar oxidation products remained strongly adsorbed on the silica matrix, the gaseous flow at the outlet of the reactor was totally free of sulfide and odorless. The best results in term of yield and initial rate of degradation of DMS were obtained with DBTP containing xerogels. Moreover, as these materials were reusable without loss of efficiency and sensitizer photobleaching after a washing regeneration step, the concept of recyclable sensitizing materials was approved, opening the way to green process.

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1. Introduction

Despite their great interest, oxidation reactions performed with molecular ground state oxygen, $^3\text{O}_2$, are limited by its weak reactivity under usual conditions. Numerous studies are thus devoted to the development of methods generating *Reactive Oxygen Species* (ROS) able to react with a large number of compounds and possibly using ground state oxygen as the reactant. Photosensitization is one of the most versatile and often used methods: one can talk of *sensitized photo-oxygenation* [1]. In most cases, if the excited singlet or triplet state of the photosensitizer (PS) is a strong enough oxidant (*i.e.* a good electron acceptor, A), it may react with an electron donor D to yield a radical-cation $\text{D}^{\bullet+}$ (Fig. 1). Then, depending on the redox potential of the ground state PS, type I mechanism may lead to the formation of the superoxide radical anion, $\text{O}_2^{\bullet-}$, by reducing ground state molecular oxygen.

Alternatively, dehydrogenation of the radical-cation $\text{D}^{\bullet+}$ leads to radical species, able to react unselectively with ground state oxygen. The type II photo-oxidation mechanism involves the formation of singlet oxygen, $^1\text{O}_2$, in its highly reactive $^1\Delta_g$ (and unstable $^1\Sigma_g^+$) states, issued from the triplet state of the PS (Fig. 2), itself arising

from inter-system crossing (ISC) from the PS singlet state. Singlet oxygen is an electrophilic species, reacting readily with electron-rich compounds such as activated double bonds or sulfides and toxic for *Escherichia coli* and similar microorganisms [2].

Sensitized photo-oxygenation may be considered as a “Green Chemistry” process, since the light energy absorbed by the PS is usually in the visible range, the only reactant is air or oxygen, and the reaction may be carried out in various media including water. Further advantages are gained when PS's are embedded or grafted on an inert support, in order to control aggregation and self-quenching of the dye [1,3] to increase its photostability, to separate the photoactive compound from the other reactants and products, to enable the use of solvents where PS's are poorly soluble or to carry out solvent-free reactions (gas–solid interface). Hence, the development of stable “photo-sensitizing materials” is an active research field, with numerous applications including [4,5]:

- Oxidation reactions of high-added value products under mild conditions for fine chemicals synthesis
- Wastewater treatment
- Bactericidal treatments (Photodynamic Inactivation, PDI)
- Photodynamic therapy (PDT)

For all these applications, the photosensitizer has to be deposited, embedded or grafted on different supports. In this way, it is possible:

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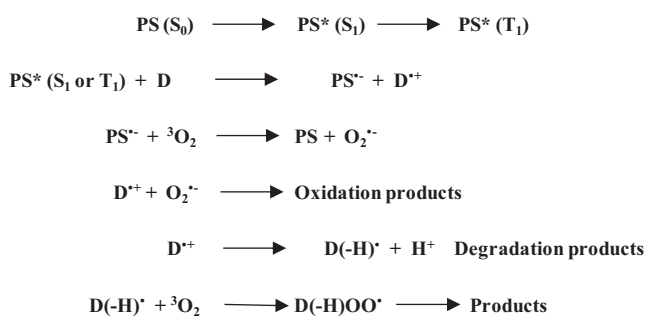


Fig. 1. Mechanism of photoinduced electron transfer reactions (Type I mechanism).

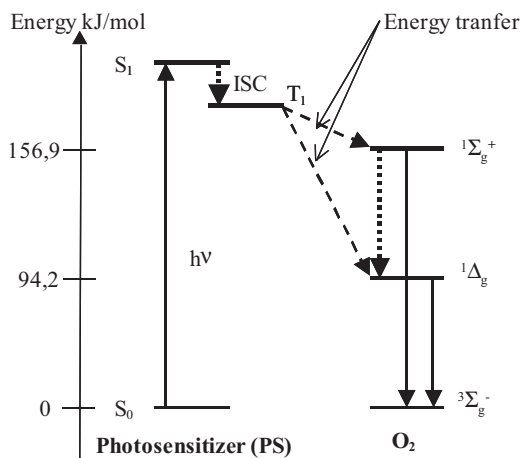


Fig. 2. Singlet oxygen formation by energy transfer. ISC: Inter System Crossing.

- to tune the absorption range by proper choice of the sensitizer
- to tune the oxidation properties (electron-transfer from redox properties of the PS with formation of radical intermediates, or energy transfer with singlet oxygen formation).
- to use various kinds of supports (silica, alumina, polymers, zeolites, layered double hydroxides (LDH), cellulose, dendrimers, carbon nanotubes...) with different macroscopic forms (films, powders, beads, glasses, fibers), specific surface area, transparency, ...

Recently, we initiated a research program to investigate the use of nanoporous silica monoliths as transparent and porous matrices for PS immobilization. These stable hybrid microreactors were shown to be an efficient tool for production of singlet oxygen and photochemical transformations. In the following, we will describe the preparation by a sol-gel process, characterization and photooxidative properties of several kinds of nano-porous silica materials containing four different supported sensitizers (Fig. 3): an anthraquinone derivative (anthraquinone-2-carboxylic acid, ANT **1a**, R=COOH), an acridine derivative (Acridine Yellow, AY), a phenazine derivative (Neutral Red, NR) and a laboratory made dicyano derivative, 9,14-dicyanobenzo[b]triphenylene 3-carboxylic acid (DBTP **2a**, R=COOH) [6].

Anthraquinone derivatives (ANT) and dicyano derivatives such as DBTP, with R=H or COOH are known to produce singlet oxygen in good yields [7]. However even if their absorption spectrum presents a maximum (for DBTP [6]) or a weak n-π* band (for ANT [8]) at 420 nm, optimal use of visible light implies a shift of these spectra towards longer wavelengths. We compared their oxidative properties with those of other sensitizers, well known for singlet oxygen production in good yields and for their maximum absorption at longer wavelengths (450 nm for AY [9] and 441 or 533 nm for

NR [9,10]). In order to improve the stability of the sensitizing materials, the PS were covalently bound to silica by various synthetic procedures.

2. Experimental

2.1. Preparation of materials

Covalent grafting of ANT and DBTP to silica was carried out either in two steps (SG1 monoliths) or in a one pot process (SG2 monoliths). In the first case, the xerogel was functionalized *in situ* with amino or isocyanate groups in a one-pot procedure by using a mixture of tetramethoxysilane (TMOS) and (3-aminopropyl)triethoxysilane (APTES) or (3-triethoxysilyl)propyl isocyanate (TEOSPI) directly in the sol composition.

For the synthesis of SG1-AY and SG1-NR, isocyanatopropyl silica was first prepared by adding 290 μL of TEOSPI (1.2 mmoles) to a sol made of methanol (24 mL, 0.6 mol), 17.5 mL of TMOS (0.12 mol) and 8.5 mL of water (0.47 mol). After stirring at room temperature for 2 min, the sol was pipetted into 1 mL molds. The molds were closed and placed in an oven at 60 °C for 10 days. The stoppers were then removed and the oven temperature decreased to 30 °C for 10 days. Drying was then carried out at 60 °C for 6 h, then at 80 °C for 2 days. The ratio TMOS/MeOH/H₂O was 1/5/4 and 1% of isocyanatopropyl groups was grafted. The grafting of AY or NR was then achieved by heating a 10⁻³ mol L⁻¹ solution of the PS in THF with isocyanato functionalized silica monoliths during 24 h at 75 °C. Silica monoliths were then washed in a Soxhlet extractor with dichloromethane to remove ungrafted PS.

The preparation of SG1-DBTP followed the same procedure and was already described [3].

Clear and crack-free silica monoliths SG2-ANT and SG2-DBTP were obtained by direct incorporation of the silylated derivative of DBTP, **2b** [3] or ANT, **1b** [11] (R=CO-NH-(CH₂)₃-SiOEt₃) in the sol composition mixed with TMOS. The molar ratio TMOS/MeOH/water was 1/5/4. Solutions of **2b** or of **1b** in MeOH (concentration 3 × 10⁻³, 3 × 10⁻⁴ and 3 × 10⁻⁵ mol L⁻¹, respectively) to prepare monoliths 1.0 × 10⁻⁶, 1.1 × 10⁻⁷ and 1.1 × 10⁻⁸ mol g⁻¹) were added to a mixture of water and TMOS. The solution was stirred with a magnetic stirrer for 2 min and the same condensation-drying procedure as previously was then followed.

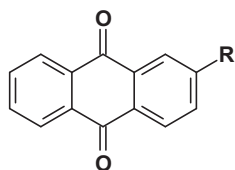
2.2. Analytical equipment

Nitrogen adsorption and desorption isotherms of the silica monoliths were measured at 77 K on a Micromeritics ASAP 2010 Micropore nitrogen adsorption apparatus. The absorption and the diffuse reflectance spectra (DRUV) were recorded with a double beam Cary 5000 spectrophotometer in steps of 0.5 nm in the range 300–600 nm using a 1 cm quartz optical cell (Hellma) or an 11 cm diameter integrating sphere with a custom-made powder holder. Teflon (Aldrich, 55 μm) was used as reference [12]. The DRUV spectra were analyzed according to the Kubelka-Munk model [13], describing light propagation in scattering media with only two parameters: an absorption coefficient, *K* and an isotropic scattering coefficient, *S* (which both have units of cm⁻¹).

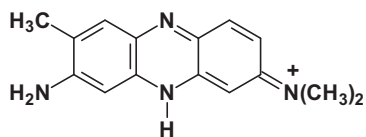
$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

With this model based on simple assumptions, the absorption coefficient *K* of the system, is proportional to the molar absorption coefficient ε(λ) (L mol⁻¹ cm⁻¹), and to the concentration *C* (mol L⁻¹) of the compound.

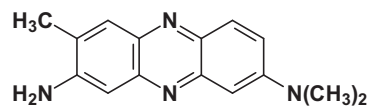
Corrected steady-state emission and excitation spectra were measured using a photon counting Edinburgh FLS920 fluorescence



Anthraquinone-2-carboxylic acid, (ANT) R = COOH (**1a**), R = CO-NH-(CH₂)₃-SiOEt₃ (**1b**)

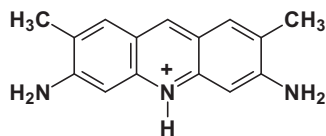


Cationic AYH⁺

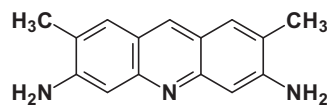


Neutral AY

Acridine Yellow (AY)

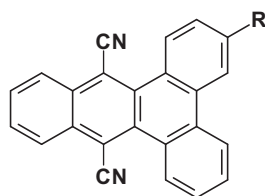


Cationic NRH⁺



Neutral NR

Neutral Red (NR)



9,14-dicyano benzo[b]triphenylene (DBTP) **2a**: R = COOH, **2b**: R = CO-NH-(CH₂)₃-SiOEt₃

Fig. 3. Formula of the PS used for the synthesis of the sensitizing materials.

spectrometer equipped with a Xe lamp. Fluorescence spectra of the powdered samples were recorded on powder adhering to sticky tape (negligible fluorescence), in 90° geometry.

2.3. Gas phase photochemical reactors

The scheme of the single-path flow reactor used for the gas-phase photo-oxidation experiments was already described [3,7,11]. Briefly, a stable DMS concentration was delivered by a thermoregulated diffusion cell to which a mass flow-meter supplied a constant flow of synthetic air (AIR LIQUIDE, Alphagaz1). The gas flowed through a cylindrical pyrex reactor (internal diameter 1.5 cm) thermoregulated at 20 °C and closely packed with about 1.2 g of the photocatalytic materials. The pyrex reactor was located inside a modified horizontal Rayonet® reactor, with fifteen RPR-4190 lamps (emission maximum at 420 nm for DBTB, ANT and AY materials), or RPR-5750 lamps (emission maximum at 575 nm for NR materials). The gas outlet was directly sampled by a pneumatic valve located on the injection port of a VARIAN 3800 chromatograph (Chrompack column CPSil-5CB 30 m, 0.25 mm, 1 μm). The gas flow was analyzed every 10 min and the concentration of DMS and of

its oxidation products was thus followed during the whole experiment. Oxidation products were first identified by comparison with pure standards or analyzed by GC-MS. Alternatively, a Varian CP-4900 micro-GC with a thermal conductivity detector was used to detect sulfur dioxide, carbon dioxide or water in the effluent. Finally, the materials after irradiation were sonicated for 30 min in acetonitrile. The acetonitrile solution was analyzed by GC for identification and quantification of desorbed organic products.

3. Results and discussion

3.1. Preparation of supported PS

The general procedure to obtain transparent and porous silica monoliths via sol-gel synthesis with or without embedded photosensitizers has already been described [3,11]. This synthetic method leads to class I hybrid materials without chemical link between the organic PS and the inorganic matrix. Washing of those materials in a solvent where the PS is soluble leads to the solubilization of the organic molecule in the solvent. Thereby in order to get reusable photo-active hybrid materials, the synthesis

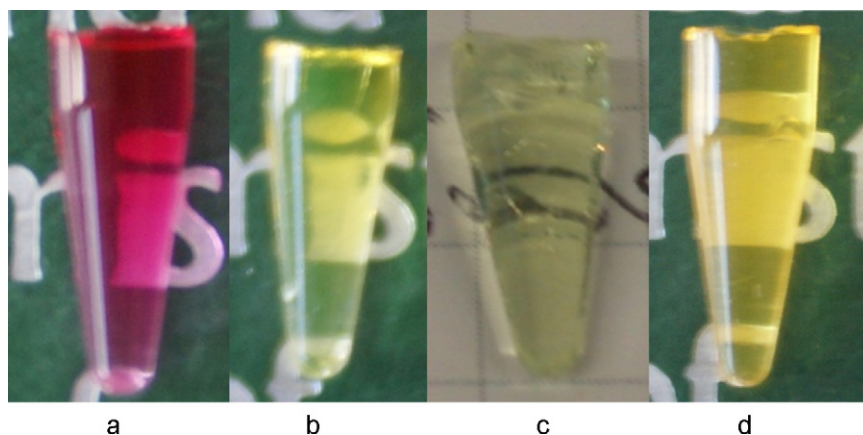


Fig. 5. Pictures of the monoliths (a) SG1-NR, (b) SG1-AY, (c) SG2-DBTP $1 \times 10^{-6} \text{ mol g}^{-1}$ and (d) SG2-ANT.

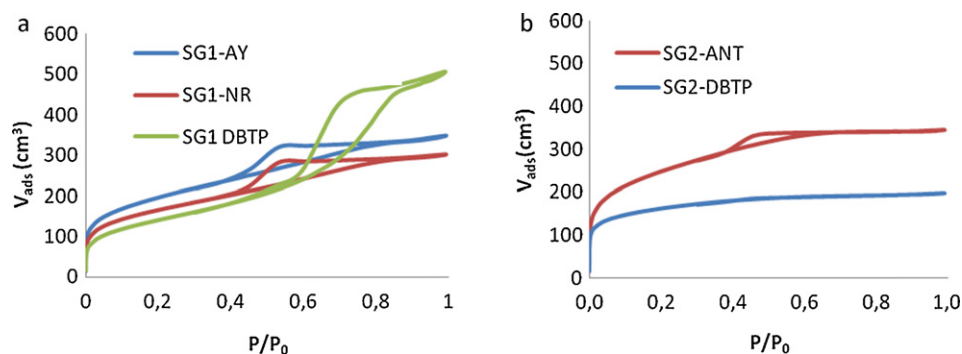


Fig. 6. N_2 adsorption–desorption isotherms of (a) SG₁ materials and (b) SG₂ materials at 77 K.

featureless bands with a maximum at 470–490 nm, to be compared with the broad emission spectrum in methanol (490–510 nm) [6].

Ma et al. already showed that the insertion (or encapsulation) of sensitizers inside silica matrices does not affect their general spectroscopic behavior [15], while Lacombe et al. demonstrated that the electronic spectra of the sensitizer in silica are comparable to those in polar solvent [3]. However, to the best of our knowledge, it is the first time that hybrid materials containing acridine or phenazine are studied. The spectrum of SG1-AY presented a broad maximum between 447 and 453 nm (Fig. 7b) in agreement with

the dye absorption in acetonitrile (453 nm, Table 2) or in methanol (457 nm, Fig. 7a). However, as the excitation spectrum did not coincide with the reflectance one (Fig. 9a), the presence of several species was assumed. Acridine yellow exists in aqueous solution as a monomer absorbing at 437 nm and as dimers with a characteristic maximum at 464 nm [16]. As we only observed a broadening of the DRUV band of SG1-AY with a maximum at 448 nm without significant shift, we excluded the presence of dimers. In solution, the absorption spectrum of AY also varies with the pH ($\text{pK}_a \sim 9.9$): a strong band at 440 nm is observed in acid medium and a smaller

Table 1

BET-equivalent specific surface area S_{BET} , porosity, volume distribution and mean size of the pores, determined by N_2 porosimetry of the silica monoliths.

Material	PS	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Surface (%)		Volume (%)	
			Microporous	Mesoporous	Microporous	Mesoporous
SG1	AY	706	80	20	35	65
	NR	593	73	27	30	70
	DBTP	507	34	64	13	87
SG2	DBTP	665	96	4	57	43
	ANT	889	79	21	42	58

Table 2

Absorption and fluorescence spectral properties of the PS in the monoliths in CH_3CN (between brackets), singlet energy state (eV).

Material	PS	λ_{abs} (nm)	λ_{em} (nm)	E_s (kJ mol^{-1})
SG1	AY	448 (453 [9])	502 (489 [9])	267
	NR	411 (441 [19,24])	^a (561 [19])	291
	NRH ⁺	532 (533 [18])	590 (601 [18])	225
SG2	DBTP	421 (414.5 [6])	470 (485 [6])	284
	DBTP	418	489	286
	ANT	328 (323)	–	263
		380–500 (370–435 [8])		

^a Non recorded.

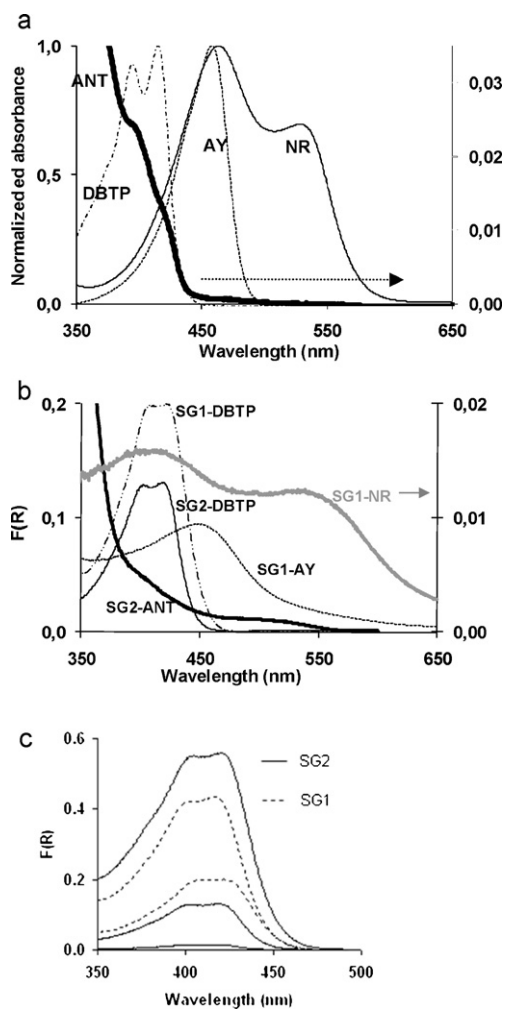


Fig. 7. UV-vis spectra (a) in MeOH solution of the various PSs; (b) diffuse reflectance (DRUV) spectra of the monoliths containing [ANT] = $1.1 \times 10^{-6} \text{ mol g}^{-1}$, [AY] = $10^{-7} \text{ mol g}^{-1}$ and [NR] = $1.1 \times 10^{-8} \text{ mol g}^{-1}$; (c) diffuse reflectance (DRUV) spectra of SG1-DBTP with DBTP at different concentration (3×10^{-7} and $8 \times 10^{-7} \text{ mol g}^{-1}$) and SG2-DBTP (1.1×10^{-8} , 1.1×10^{-7} and $1.0 \times 10^{-6} \text{ mol g}^{-1}$) monoliths.

one at 390 nm under basic conditions [17]. From the broad shape of the DRUV band, we thus assumed that the monolith contained both neutral AY and cationic AYH^+ (Fig. 3), in agreement with the several previous species deduced from the excitation spectra.

In solution, the fluorescence emission spectra of AY showed one peak between 480 and 510 nm and were slightly red shifted when

increasing the solvent polarity [9]. The maximum at 502 nm in the monolith (Fig. 9b) is consistent with the values observed in solution.

In aqueous solution, Neutral Red is involved in an equilibrium between the protonated form NRH^+ and a deprotonated form NR (Fig. 3), with a pK_a of 6.8 [18]. The absorption maxima of NRH^+ varied from 534 to 541 nm and the absorption maxima of NR from 430 to 459 nm. The spectrum in MeOH with two maxima at 528 and 463 nm (Fig. 7a) indicated the presence of both species. In the DRUV spectrum of SG1-NR, two broad maximum at 410–430 and 530–550 nm were observed, probably corresponding to neutral NR and charged NRH^+ (Fig. 7b). From the molar extinction coefficient of both species [19], and from the higher intensity of the band assigned to NR, it was concluded that the neutral form was the main one in the monolith. The fluorescence emission spectra of SG1-NR (Fig. 8b) exhibited broad and featureless bands with a maximum at 590 nm, in agreement with the presence of both neutral NR and charged NRH^+ .

SG2-ANT showed, as ANT in methanol, a strong π - π^* absorption band at 328 nm and a much weaker n - π^* between 380 and 550 nm (Fig. 7a) [8].

To summarize, no significant differences between the UV spectra of the PSs in MeOH and the DRUV spectra of the monoliths were noticed.

3.3. Photo-oxidation results

Sulfur derivatives such as dimethylsulfide (DMS) are nauseous compounds produced by the paper industry. DMS is a low boiling point (37.5°C) clear and flammable liquid with a low olfactory detection limit (1.2 ppb). It may cause eye, skin and respiratory tract irritation and is harmful if swallowed. Sulfides are known to very easily add singlet oxygen, leading to odorless and polar compounds such as dimethylsulfoxide (DMSO) and dimethylsulfone (DMSO_2) [20]. DMSO is a stable, not hazardous, high boiling point (189°C) and colorless liquid with low acute and chronic toxicity for animal, plant and aquatic life. DMSO_2 is a very stable, extremely non-toxic and with a still higher boiling point liquid (248°C). Hence, any green process to destroy and convert sulfides to their harmless oxidation products is highly desired (as for instance in the case of Mustard gas ($\text{ClCH}_2)_2\text{S}$).

3.3.1. General procedure

We only used air as reactant and visible light as activation to carry out this *solvent-free* reaction. The reactions were carried out in a flow reactor with typical residence time of few seconds (1–5 s). The flowing gas was continuously analyzed and the concentration of the starting pollutant and of products was monitored by GC. The concentration of the pollutant in the flowing gas was 100–180 ppmv. In each case about 1.2 g of the sensitizing material

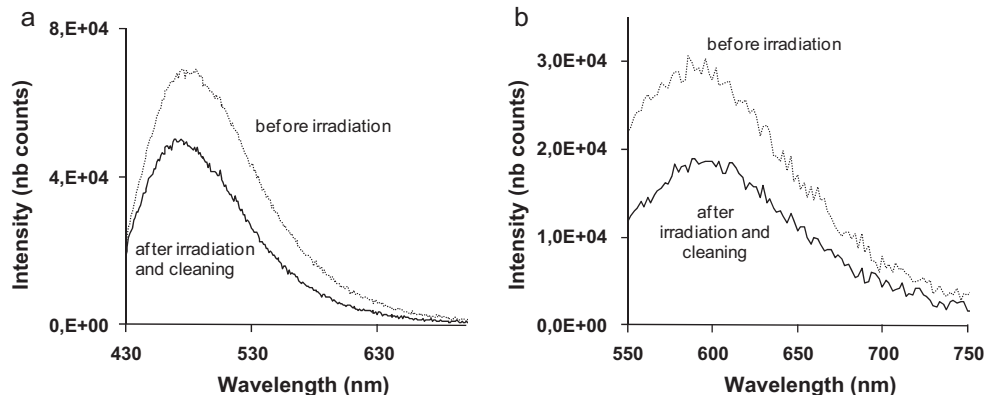


Fig. 8. Fluorescence emission spectra before and after irradiation and CH_3CN washing/drying of (a) SG1-DBTP ($\lambda_{\text{ex}} = 420 \text{ nm}$) and (b) SG1-NR ($\lambda_{\text{ex}} = 530 \text{ nm}$).

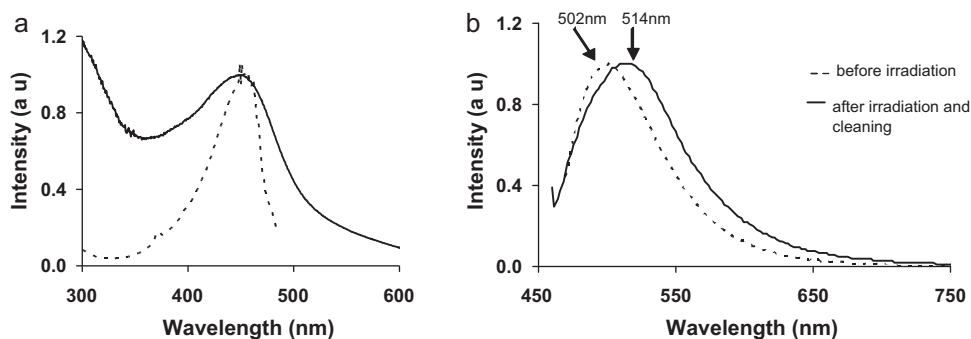


Fig. 9. Fluorescence spectra of SG1-AY (a) excitation ($\lambda_{\text{ex}} = 457 \text{ nm}$, $\lambda_{\text{em}} = 502 \text{ nm}$) and (b) emission before and after irradiation and CH_3CN washing/drying ($\lambda_{\text{ex}} = 450 \text{ nm}$).

was used. For a typical experiment, in the first part of Fig. 10 (step I), DMS was adsorbed in the porous material until the initial concentration of DMS (dotted line) in the effluent was reached. Once the material was saturated with the pollutant, the lamps were switched on (step II) and the DMS concentration in the effluent decreased dramatically. Traces of oxidation products such as DMSO and DMSO_2 were observed in the gaseous flow (not shown here). After 18 h, the lamps were switched off (step III) and the fast increase of DMS concentration back to the inlet value was observed. The percentage of DMS degradation was determined graphically (dashed area). The polar oxidation products, mainly adsorbed on silica, were determined at the end of the reaction, by washing the monoliths in acetonitrile and analyzing the obtained solutions by GC. The monoliths were then dried under vacuum, analyzed by spectroscopy and re-used.

The results obtained under these conditions are reported Table 3 according to the general presentation:

- PS amount in the material (mol g^{-1}),
- percentage of DMS degradation: integrated difference between the equilibrium concentration in the dark and the measured concentration during the 24 h irradiation time (dashed area in Fig. 10),
- slope of the concentration curve after switching on the lamps (ppm h^{-1}),
- oxidation products (%) desorbed from the xerogel after acetonitrile washing and GC analysis of the organic extract.

For the SG2 xerogels obtained by one-pot synthesis, two parameters were studied: the influence of the sensitizer (DBTP and ANT) and the influence of the PS concentration for SG2-DBTP.

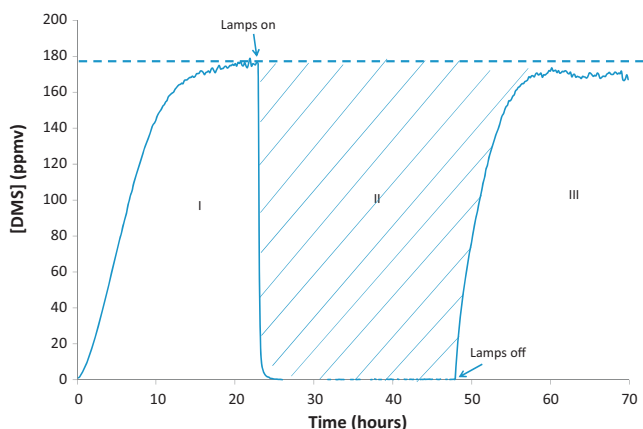


Fig. 10. Concentration of DMS in the photoreactor exhaust gas during a typical experiment. See text for explanations.

3.3.2. Results and discussion

With all the studied materials, DMS photo-oxygenation yields varied between 43 and 94%, with the detection of dimethylsulfoxide (DMSO) and dimethylsulfone (DMSO_2) as main oxidation products (desorbed in acetonitrile from the materials after irradiation, Table 3).

In order to compare the results, two parameters have to be taken into account: the PS concentration and the light absorption at the maximum wavelength emission of the lamps (420 or 575 nm, Table 2).

The best results were obtained with DBTP containing materials with 94% yield of DMS photo-oxygenation in the case of SG1-DBTP. It may also be concluded that a high DBTP concentration did not improve significantly the photo-oxygenation yield, either with the SG1 or SG2 monoliths. The initial slope of DMS concentration was more sensitive to DBTP concentration (and thus to light absorption) and to the nature (SG1 or SG2) of the monolith, in possible relation with the highest mesoporosity of the SG1 type materials (Table 1).

SG2-ANT was much less efficient than SG2-DBTP, at the same concentration ($10^{-6} \text{ mol} \times \text{g}^{-1}$), in agreement with a much smaller $F(R)$ at 420 nm (0.02 and 0.6, respectively).

For a PS concentration of the same order of magnitude ($10^{-7} \text{ mol} \times \text{g}^{-1}$) and roughly the same light absorption at 420 nm ($F(R)$ 0.08 and 0.13, respectively), SG1-AY is much less efficient than SG1-DBTP (93 and 74%, respectively).

Post-grafted SG₁ materials containing DBTP, Acridine Yellow or Neutral Red allowed comparing the efficiency of each sensitizer grafted to the silica matrix. In this case, the sensitizer concentration depended on the yield of the grafting reaction between the functionalized silica and the PS derivative and was determined by DRUV spectroscopy. It was found to vary between 10^{-8} (SG1-NR) and 8×10^{-7} (SG1-DBTP) mol g^{-1} . Under our conditions, SG1-NR and SG1-AY were much less efficient than SG1-DBTP (Table 2). The very poor results obtained in the case of SG1-NR may be explained by the weak absorption of the material between 450 and 650 nm compared to the other materials (Fig. 7b) [21].

A slight evolution in the DMSO/ DMSO_2 ratio may be noted in Table 3. Generally sulfoxide is found as the major product (DMSO/ DMSO_2 ratio: 70/30), as often observed for solution reactions [22]. This ratio is reversed for both SG1-DBTP and SG1-AY monoliths and decreases for the less loaded SG2-DBTP relative to the more concentrated ones.

In any case, whatever the material, singlet oxygen formation was deduced from the oxidation products (DMSO and DMSO_2), with sensitizer concentration in the silica xerogels between 10^{-8} and $10^{-6} \text{ mol g}^{-1}$, corresponding to a maximum of 1.5×10^{-8} to 1.5×10^{-6} moles of sensitizer in the reactor during each experiment. Compared to the amount of pollutant introduced in the gas phase (about 6×10^{-4} moles over 24 h), the ratio between pollutant and sensitizer varied between one molecule of PS for 40,000–400

Table 3

F(R) of the monoliths at 420 nm (except otherwise stated), yield of DMS photo-oxygenation, initial slope of [DMS] concentration under irradiation and products distribution ratio.

Xerogel	PS	[PS] (mol g ⁻¹)	F(R) ₄₂₀	DMS photo-oxygenation (%)	Initial rate of [DMS] photo-oxygenation (ppm h ⁻¹)	Oxidation products after acetonitrile extraction (%)	
						DMSO	DMSO ₂
SG1	NR	1 × 10 ⁻⁸	0.01 ^a	43	10	74	25
	AY	1 × 10 ⁻⁷	0.08	74	36	40	56
	DBTP	3 × 10 ⁻⁷	0.20	93 (96) ^b	100 (173) ^b	29 (47) ^b	70 (53) ^b
SG2	DBTP	8 × 10 ⁻⁷	0.43	94	144	36	63
		1.1 × 10 ⁻⁸	0.01	83	61	55	42
		1.1 × 10 ⁻⁷	0.13	81	86	70	30
	ANT	1.0 × 10 ⁻⁶	0.56	89	98	70	30
		1.0 × 10 ⁻⁶	0.03	58	35	72	28

^a F(R) at 575 nm.

^b Results obtained after four cycles irradiation/washing/drying.

molecules of pollutant. It should be emphasized that for the most efficient SG1 and SG2-DBTP materials, the reaction was stopped after 24 h without any activity loss and could have been continued for several days, enhancing the previously calculated efficiency by several order of magnitude.

According to these results, it appears that SG2-DBTP, and even more SG₁-DBTP materials (two-step synthesis), are the best candidates for the photo-oxidation of gaseous compounds such as DMS through singlet oxygen generation. In the following we checked the possible re-use of such materials.

3.3.3. Recycling xerogels

For the purpose of analysis, the polar oxidation products, mainly adsorbed on silica, were determined at the end of the reaction, by washing the monoliths in acetonitrile and drying under vacuum before re-use. However, as DMSO is very soluble in water, it is also possible to use first water for desorption and second an alcohol in order to get rid of less water soluble reaction products and washing water. In any cases the amount of washing water/solvent are low and this step is to be considered as the regeneration of the materials, after the solvent free oxidation step. Although fluorescence emission spectra of the powdered samples could not give quantitative data (it is thus impossible to rely the intensity decrease of the bands only to concentration drop, as experimental parameters are not easily mastered for powdered samples), the spectra of SG1-AY (Fig. 8) and SG1-NR (Fig. 9) before and after irradiation already indicated that the PS were roughly stable under irradiation, and that the electronic spectra of the PS were recovered after reaction, desorption of the oxidation products in acetonitrile and drying at 373 K under reduced pressure. With the SG1-AY monoliths, a slight shift to longer wavelength was observed after irradiation in the presence of dimethylsulfide (DMS), washing of the monolith in acetonitrile and drying (Fig. 8b), probably due to remaining polar oxidation products not completely removed after the washing procedure. However the dye was still observed in the monoliths SG1-AY and SG1-NR (Fig. 9) after the reaction and photobleaching was not measurable.

The emission/excitation spectra of SG1-DBTP, after four of cycles irradiation/washing/drying at 373 K under reduced pressure (Fig. 8a) were unchanged showing that the sensitizer was stable under these conditions and that no photo-bleaching or leaking of DBTP occurred. With the recycled monoliths, the photo-oxygenation yields were similar (Table 3), while the initial rate of DMS photo-oxygenation was greater and the DMSO/DMSO₂ ratio decreased. One explanation is the possible change of the environment, like relative humidity and/or polarity inside the monoliths, as already demonstrated by Clennan *et al.* during oxidation of sulfide in a zeolite matrix [23].

It is also noteworthy to point out that no trace of DBTP was found in the solutions after the washing process. It may be concluded that DBTP remained unaffected by these recycling process and that the molecule is strongly anchored to the silica matrix. This point further validates the concept of a reusable material.

4. Conclusion

New xerogels containing various grafted photosensitizers were prepared. The compared PS were well-known anthraquinone derivatives, commercial Neutral Red (a phenazine derivative), Acridine Yellow and a laboratory-made dicyano aromatics (DBTP). These xerogels were used as nanoporous microreactors for gas/solid solvent-free photo-oxygenation of dimethylsulfide (DMS) using visible light and air as the sole reactant. Electronic spectroscopy proved to be a useful tool for monitoring the PS concentration and form in the powdered silica, and to evaluate the materials' evolution under irradiation.

All these PS containing monoliths were efficient for gaseous DMS oxidation, leading to much harmless sulfoxide and sulfone in varying ratios. As these polar oxidation products remained strongly adsorbed on the silica matrix, the gaseous flow at the outlet of the reactor was totally free of sulfide and odorless. The best results in term of yield and initial slope of DMS concentration were obtained with DBTP containing xerogels. Moreover, as these materials are reusable after a regeneration step consisting of washing them in a suitable solvent (including water), without loss of efficiency and sensitizer photobleaching, the concept of recyclable sensitizing materials is proved. In other words, this solvent-free process using air and visible light allows the transformation of volatile and toxic product to heavier and harmless oxidation products, which can be released afterwards from the materials by washing in minimum amounts of solvents.

Better insight in the reaction mechanisms is sought, even if singlet oxygen is most probably involved. Quantum yields of singlet oxygen formation with the various PS in the silica matrix are currently investigated by phosphorescence emission microscopy.

Applications of these kinds of grafted, stable materials are to be found for the solvent-free oxidation of gaseous products, for the solution oxidation of high added value compounds (fine green chemistry), and for water disinfection using air as the only chemical and visible light as activation. As long as the materials can be recycled, green processes are thus made possible.

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