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Photocatalytic synthesis of thio-organic compounds: case study of propan-1-thiol

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Abstract

Photocatalytic synthesis of propan-1-thiol has been performed at room temperature under dynamic conditions by addition of H_2S on propene in contact with illuminated TiO_2 or CdS catalysts. Both photocatalysts were found to be active and selective in this reaction. Propan-1-thiol was selectively obtained according to a reaction mechanism implying photogenerated $SH^{\bullet}$ radicals. This work illustrates the potentialities of photocatalysis in the field of thiochemistry.

Keywords: Heterogeneous photocatalysis; Thiochemistry; Propan-1-thiol; Thiophotocatalysis; Titanium dioxide; Cadmium sulfide

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1. Introduction

The interest of heterogeneous photocatalysis has recently been growing particularly in the field of water and air decontamination in which the photocatalyst is able to oxidize organic pollutants to CO_2 with oxygen from the air [1]. If the oxidative degradation of molecules in water and air purification is the main application of photocatalysis [2,3], the synthesis of organic compounds can also be performed [4]. The wide applicability of semiconductor-mediated photocatalysis for functional group transformations of organic compounds has been demonstrated for substitution, addition, oxidation, reduction, dehydrodimerization and isomerization [5]. These reactions have mainly been performed with organic molecules involving C–C, C–O or C–N bonds and, in a small extent, on sulfur-containing molecules. In the field of thiochemistry, mercaptans are increasingly used as intermediates for the synthesis of agrochemicals, pharmaceuticals, petrochemicals, lubricants, cosmetics and gas odorants. Consequently, new synthetic routes for mercaptans are to be developed. Primary mercaptans are usually prepared either by heterogeneous catalysis from *n*-alcohols or by photo-assisted addition of H_2S to α-olefins [6,7]. For secondary and tertiary thiols, the addition of H_2S on the olefinic double bond by acid catalysis is preferred since the dehydration of the alcohol also produces undesired products.

Only few examples of photocatalytic synthesis of thio-compounds can be found in the literature. Reduction of disulfides of bis(2-dipyridyl)disulfide for the synthesis of 2-mercaptopyridine on catalyst has been reported [8]. Additionally, the photoreactivity of H_2S in contact with photocatalysts such as CdS, ZnS and TiO_2 has been investigated for H_2S oxidation [9], sulfur recovery or hydrogen production [10,11].

The present study is aimed at investigating the photocatalytic synthesis of mercaptans in the gas phase by direct reaction of an olefin with H_2S. For propan-1-thiol, only this route can be envisaged because in the heterogeneous catalytic process, propan-2-thiol is mainly formed. In photochemistry (i.e. without a photosensitive solid catalyst), a secondary reaction producing a large amount of alkyl sulfide is also observed [12]. Presently, it is attempted to synthesize propan-1-thiol by a photocatalytic process, using either TiO_2 or CdS catalysts. In the presence of H_2S, the surface of TiO_2 gets partially sulfurized and its photocatalytic properties might be affected, whereas CdS should not be transformed. Additionally, CdS absorbs in the visible region. Eventually, photocatalytic activity differences have been observed between these two photocatalysts with respect to the final products obtained. For instance, the synthesis of pipecolinic acid from (*S*)lysine leads selectively

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to the *S* isomer with platinized TiO_2, whereas the racemic mixture is obtained with platinized CdS [13].

2. Experimental

2.1. Preparation of the photocatalysts

The titania catalyst used was a commercial HOMBIKAT UV100 sample purchased from Sachtleben (Germany). The method of preparation of cadmium sulfide particles was similar to that employed by Ramsden and Grätzel [14]. Gaseous hydrogen sulfide was introduced in an aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (Aldrich 98%), under vigorous stirring. CdS particles were rapidly formed and separated from the solution by centrifugation before being washed out with distilled water. The yellow-orange powder obtained was used as photocatalyst without any further treatment.

2.2. Characterization of the catalysts

X-ray powder diffraction patterns were recorded with a Brucker D5500 diffractometer using Cu Kα radiation. Particle shapes and sizes were determined by transmission electron microscopy (TEM), performed with a JEOL 2010 microscope operating at 200 kV. Samples were prepared by depositing a droplet of an ethanol slurry onto a holey carbon-coated copper grid. The crystalline phases were also determined by nanodiffraction or FT image processing. The elementary analyses were obtained by using EDX spectroscopy (Link Isis). BET surface areas were measured with an automatized volumetric apparatus based on nitrogen adsorption at 77 K.

Bandgap energies were determined according to the method described by Weber [15]. UV-spectra of Kubelka-Munk function $F(R'_\infty)$ vs. wavelength of incident photon were recorded with a Perkin-Elmer Spectro Lambda 9 and were represented as $(F(R'_\infty) \times h\nu)^2$ vs. $h\nu$. The bandgap energy E_G corresponds to the intercept of the linear part of the curve with the *x*-axis.

2.3. Photocatalytic thiolation of propylene

Photocatalysed thiolation of propene was performed at room temperature in the dynamic gaseous photoreactor having a cylindrical shape [16]. The catalyst powder was spread out on a microfibre glass filter, playing the role of a photo-inert support of the immobilized photocatalytic bed. UV-irradiation of the catalyst in the presence of reactants was provided by a 125 W high-pressure mercury lamp (PHILIPS HPK 125). IR beams were removed by a water cell. A Corning cut-off filter (0–52) was chosen for the desired wavelength range, i.e. for $\lambda \geq 340$ nm. The section area of the reactor was ca. 11 cm^2. N_2 was used as the carrier gas for the gaseous mixture of propylene + H_2S, which was introduced in the head-space of the photoreactor and passed through the fixed catalyst bed before reaching the outlet. Propylene and thiol concentrations were measured by gas chromatography using a HP 5890 chromatograph equipped with a HP5 capillary column (50 m × 0.32 mm), and a flame ionization detector. The total flow rate was 18 cm^3/min, while propene and H_2S partial pressures were equal to 13 and 17 Torr, respectively (1 Torr = 133.3 Pa). Analyses were performed on-line every 7 min. The interest of such a flow reactor is to provide information on the true kinetics in initial conditions. It enables one to follow the activation/deactivation processes. Under these dynamic differential conditions, conversions were in the range of 1%. The reaction rate r (in mol s^{-1}) of thiol appearance was expressed as

$$r = FX$$

where F is the molar flow rate of propene and X the conversion. The weight of the catalyst has been optimized by varying the mass for each catalyst in order to ensure a total absorption of efficient photons [3]. In the absence of light, and/or of catalyst, it was clearly checked that no reaction occurred.

2.4. Determination of the quantum yield

The quantum yield Φ_λ was defined as the ratio of the reaction rate r to the photon flux R_λ actually absorbable by the catalyst. It is expressed either in molecules converted per second per photon absorbed per second or in moles converted per second per Einstein absorbed per second (1 Einstein = 1 mol of photons) [17]. The determination of the quantum yields in photocatalysed heterogeneous reactions present some difficulties because of the scattering and the reflection of light by the semiconductor grains. Therefore, the value determined constitutes only a minimum value [18,23]. The apparent quantum yield was calculated by assuming that all the incident photons are absorbed by the semiconductor.

The total absorbable photon flow was calculated for each semiconductor by taking into account: (i) the radiant flux (sometimes called intensity, expressed in mW/cm^2 and measured with a radiometer: ORIEL Radiant Power Meter (model 70260) equipped with a 70261 ORIEL Thermopile Detector); (ii) the spectrum of the lamp; (iii) the transmittance of the filter; (iv) the semiconductor absorption spectrum. The light flux was found maximum in the middle of the reactor and decreases along the radius of the irradiated surface. However, this maximum value has been used for the entire illuminated section area of the photoreactor.

For each band of the lamp, the monochromatic photon flow actually absorbed by the catalyst was calculated from the monochromatic radiant flow (in mW/cm^2) given by the manufacturer and by taking into account the absorbance of the solid and the transmittance of the optical filter as usually done by one of us (JMH) since many years (see for instance [20]).

Table 1
Physico-chemical properties of TiO_2 and CdS photocatalysts

	TiO_2	CdS
Bandgap (eV)	3.3	2.3
S_{BET} (m^2/g)	286 ± 4	42 ± 2
Phase proportion (%)	100% Anatase	20% Hawleite/80% Greenockite
Average size, XRD (nm)	8	14

3. Results and discussion

3.1. Physico-chemical properties of the solids

The two photocatalysts exhibit relatively high specific surface areas. The crystalline composition of TiO_2 and CdS were determined from XRD patterns (see Table 1). The sulfide photocatalyst is a mixture of cubic and hexagonal phases, whereas titania is 100% anatase. The photocatalytic activity of both CdS phases is not reported in the literature and we arbitrarily supposed that they are identical. Figs. 1 and 2 provide the TEM micrographs of the photocatalysts. These catalysts are composed of small and well-crystallized particles having a nearly spherical shape. Mean sizes were comparable to those obtained from XRD line broadening. The bandgap energies were determined from the UV-absorption spectra presented in Fig. 3. They correspond fairly well with those reported in the literature. In fact, quantum size effects for TiO_2 and CdS are expected to occur for particle sizes below 5 nm [19].

3.2. Catalytic activities

As mentioned above, the differential flow system gives directly the initial reaction rate and enables one to detect any activation/deactivation processes. In Fig. 4, the photocatalytic activities of TiO_2 and CdS under UV–visible are compared. It can be observed that catalysts necessitate an induction period of ca. 40 min to reach their optimum activities. After this activation period, the catalytic activity remains stable. Both solids are active in the thiolation of propene performed in the gas phase. As in the case of photocatalytic mild oxidation reactions, the photocatalysts exhibit high selectivities since propan-1-thiol is formed with a selectivity >99%. It has to be underlined that this selectivity is opposite to that would be expected in conventional thermo-activated heterogeneous catalysis. Actually, the reactor was heated up to 413 K and then cooled down to room temperature and illuminated. Fig. 5 clearly illustrates how thermal or photonic activation affect the selectivity of each thiol. Under illumination, the photocatalytic activity of TiO_2 is about three times higher than that of CdS. The photocatalytic properties of both solids are summarized in Table 2.

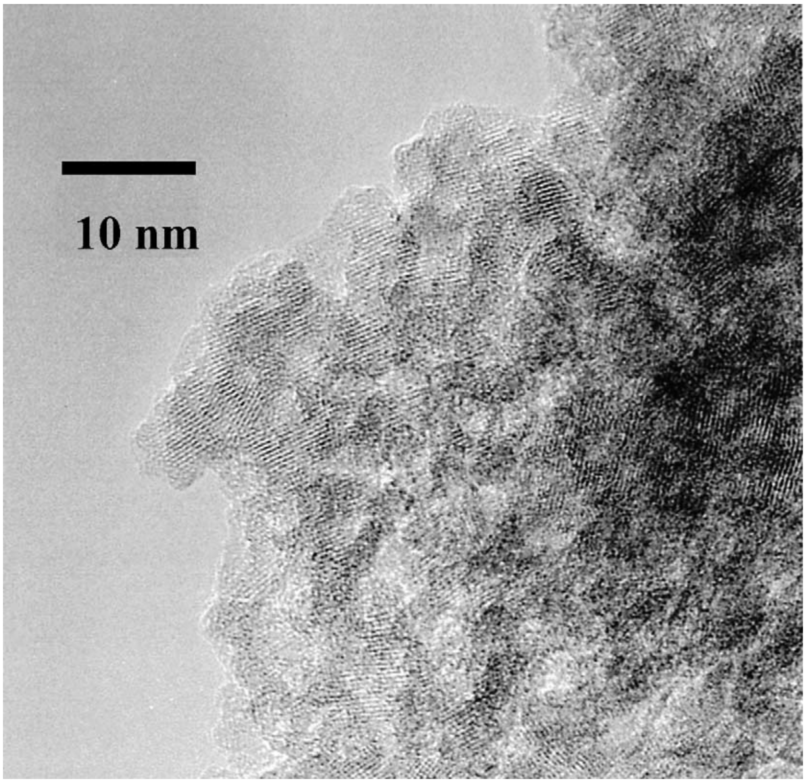

Fig. 1. TEM image of TiO_2 photocatalyst (Hombikat UV 100).

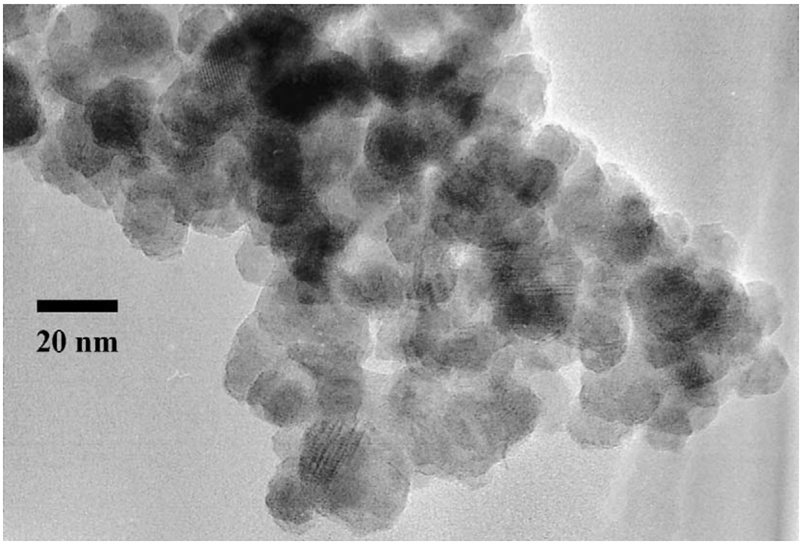

Fig. 2. TEM image of CdS photocatalyst.

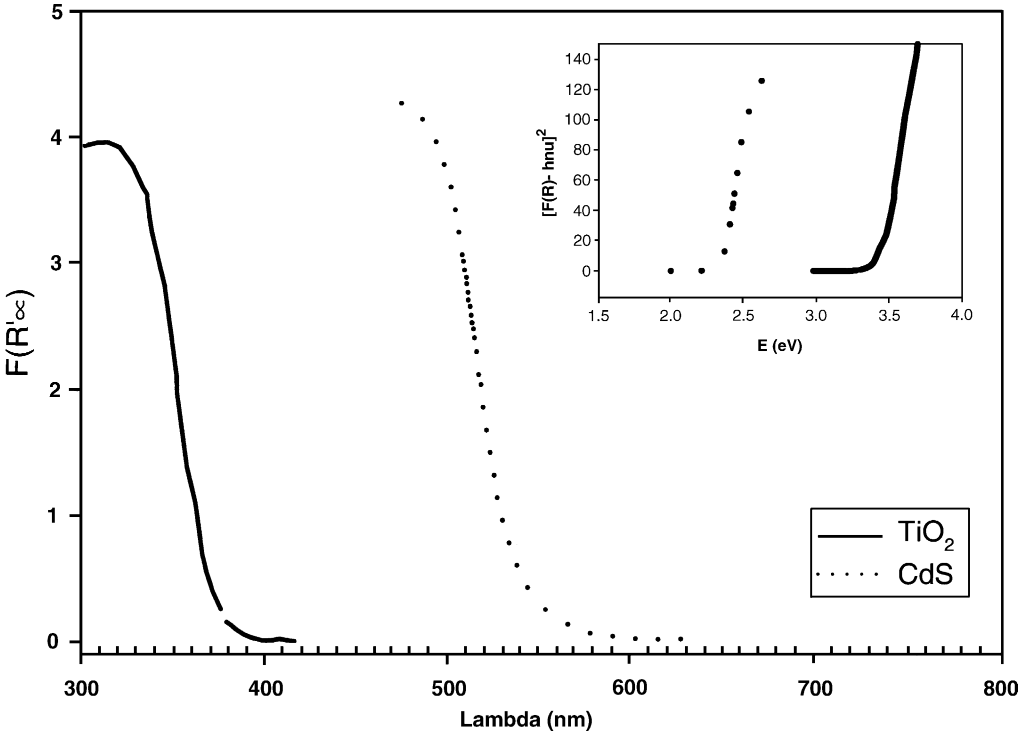

Fig. 3. UV spectral of Kubelka-Munk function $F(R)$ vs. wavelength of incident photon for TiO_2 (Hombikat UV-100) and CdS, and inset $[F(R'_\infty) \times h\nu]^2$ vs. energy.

Table 2
Photocatalytic properties of TiO_2 and CdS[a]

	TiO_2 (UV–visible)	CdS (UV–visible)
Adsorbable flux ($h\nu$/W/s)	3.8×10^{16}	7.26×10^{17}
Rate (mol/s)	1.4×10^{-9}	3.8×10^{-10}
Quantum yield	2.2×10^{-2}	3.15×10^{-4}

[a] A Corning cut-off filter (0–52) was chosen for the desired wavelength range, i.e. for $\lambda \geq 340$ nm.

3.3. Reaction mechanism

Since the behaviors of both titania and CdS are similar (with, in particular, the same very high selectivity in propan-1-thiol), this indicates that they should follow the same reaction mechanism. For titania, which is known as a powerful oxidation photocatalyst in oxygen, this implies that its surface has to adapt to thiolation conditions. This can be

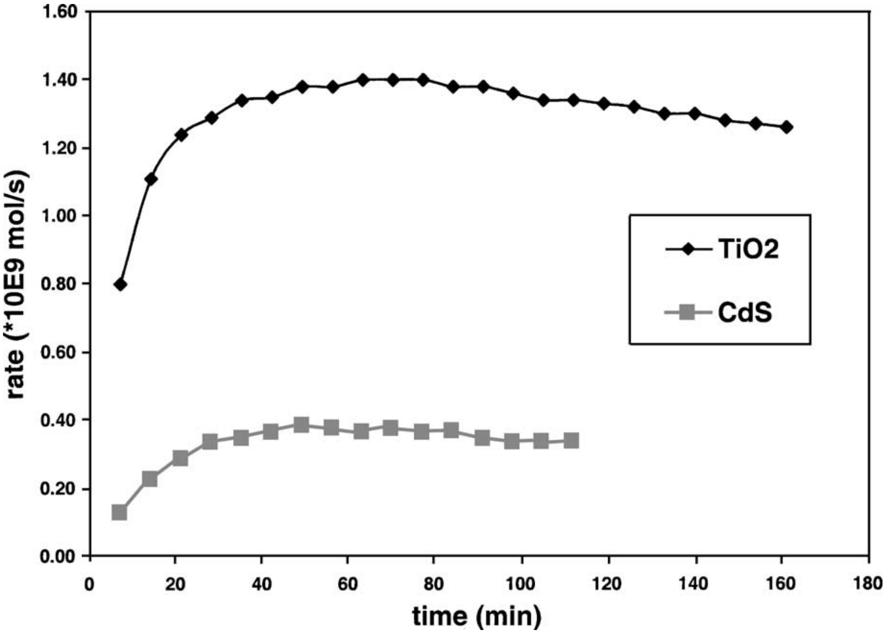

Fig. 4. CdS and TiO_2 photocatalytic activities under UV–visible light filtered by a Corning cut-off filter (0–52) for $\lambda \geq 340$ nm.

easily done at room temperature by a partial sulfidation of the surface by reaction of gaseous H_2S with the amphoteric hydroxyl groups of titania.

Under UV-irradiation, the photon absorption creates photo-electrons and holes.

$$TiO_2 + h\nu \rightarrow e^- + p^+ \quad (1)$$

Simultaneously, the hydrocarbon co-reactant adsorbs at the surface of titania. It has been shown by one of us that (i) alkanes adsorb on UV-illuminated titania at room temperature as an almost physisorbed monolayer without any electronic interaction with the solid [20] and (ii) propene was found to weakly chemisorb on titania during its mild initial oxidation into propene oxide as the initial product [21].

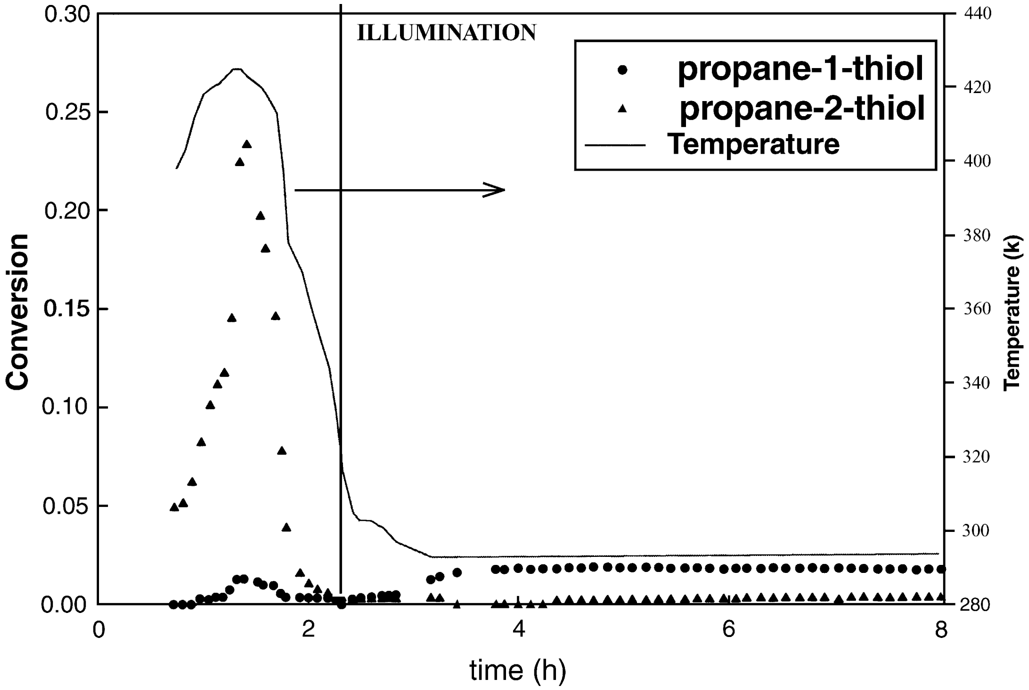

Fig. 5. Influence of thermal and photocatalytic activation on the conversion of thiols on TiO_2.

In both cases, no influence of the hydrocarbon partial pressures was observed on the electrical photoconductivity of titania, indicating that these reactants are without any electronic interaction with the irradiated solid. Propene can be considered in the present conditions as merely adsorbed

$$C_3H_{6(g)} + TiO_2 \rightarrow C_3H_{6(ads)} \tag{2}$$

The fate of the photogenerated electrical charges has to be concerned with H_2S. Because of the acidic properties of H_2S, a dissociative chemisorption can be proposed on the amphoteric sites of totally or partially sulfided surface of titania

$$H_2S + TiO_2 \rightarrow HS^-_{ads} + H^+_{ads} \tag{3}$$

The HS^- surface groups constitute good candidates for reacting with positive holes as their OH^- homologues in aqueous medium, thus generating $SH^\bullet$ radicals

$$HS^-_{ads} + p^+ \rightarrow HS^\bullet_{(ads)} \tag{4}$$

These electrophilic radicals subsequently react with the double bond of the co-adsorbed olefin to generate a new radical with the terminal position of the thiol group

$$HS^\bullet_{(ads)} + CH_2{=}CH{-}CH_{3(ads)} \rightarrow HS{-}CH_2{-}{}^\bullet CH{-}CH_{3(ads)} \tag{5}$$

This radical has to meet another radical to form a stable final molecule. No dimerization of the thiol compound was observed. The overall reaction corresponds to the addition of $SH^\bullet$ and $H^\bullet$ on the double bond of adsorbed propene. By varying the contact time, we observed that traces of propan-2-thiol are not related to the photocatalytic process itself but apparently proceeds via another activation process. For such a mechanism, the reaction would proceed through protons and SH^- addition, which is similar to the catalytic thermal activation leading to propan-2-thiol. This secondary minor process may explain the presence of traces of 2-propan-thiol in the case of cadmium sulfide but also for TiO_2 because of the partial sulfidation of the surface of the anatase particles. Under non-oxidative atmosphere, TiO_2 was found to be partially sulfided at room temperature by the displacement of surface hydroxyl groups by SH groups as evidenced by IR [22], whereas under oxidizing atmosphere these surface species are oxidized into sulfates [9]. In our non-oxidative experimental conditions, the surface of TiO_2 presents both OH and SH groups which contribute to the Brönsted acidity which promote the formation of propan-2-thiol.

Concerning CdS, the same mechanism can be applied since (i) the same selectivity in propan-1-thiol was obtained (as well as traces of and propan-2-thiol) and (ii) the sulfide nature of the catalyst is quite adapted to thiolation.

3.4. *Quantum yield*

The quantum yield ρ, defined above according to IUPAC recommendations [23], has been determined for both catalysts according to the procedure described in Section 2. Their values are given in Table 2. Whereas titania appears as only three times more active in Fig. 4, its quantum yield is 70 times higher than that of CdS. This is because of the visible photons which have been taken into account for CdS, in agreement with the UV–visible spectra in Fig. 3. To our experience, a quantum yield of 2% observed appears as quite reasonable in the gas phase using a differential flow photoreactor. It is of the same order of magnitude as that of propene oxidation [21]. Its value higher than that of CdS confirms two points: (i) titania remains the best photocatalyst and (ii) titania, owing to its own surface properties, is able to adapt to many different reaction media, presently a sulfiding atmosphere, enabling it to perform a thiolation reaction with a better yield than that of a sulfide. These results, which were mainly exploratory, clearly indicate that a new area in titania's photoactivity can be developed in thiochemistry (so-called thiophotocatalysis).

4. Conclusion

The present work illustrates a new potential for photocatalysis in the synthesis of thio-compounds. The ability of TiO_2 or CdS to perform the synthesis of mercaptans has been clearly demonstrated. Both catalysts are highly selective in the formation of propan-1-thiol, which was not the product expected in a heterogeneous catalytic system. New developments are undertaken to broaden this new thiochemical field.

Acknowledgements

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