



## A parametric study of the UV-A photocatalytic oxidation of H<sub>2</sub>S over TiO<sub>2</sub>

Angela Alonso-Tellez<sup>a</sup>, Didier Robert<sup>a,b</sup>, Nicolas Keller<sup>a</sup>, Valérie Keller<sup>a,\*</sup>

<sup>a</sup> Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), CNRS, University of Strasbourg, 25 rue Becquerel 67087, Strasbourg, France

<sup>b</sup> Saint-Avold Antenna, LMSPC, CNRS, University of Metz and University of Strasbourg, rue Victor Demange, 57500 Saint-Avold, France

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### ABSTRACT

A parametric study of the UV-A H<sub>2</sub>S photocatalytic oxidation over TiO<sub>2</sub> P25 has investigated the influence of the TiO<sub>2</sub> coating surface density, the total flow rate, the relative humidity, the temperature and the irradiance as main reaction parameters on the H<sub>2</sub>S conversion, the SO<sub>2</sub> selectivity (targeted as low as possible), the duration without any SO<sub>2</sub> release, and thus on the gas phase sulfur removal efficiency. The deepest non-illuminated internal TiO<sub>2</sub> layers – even not photocatalytically active – could play a role in adsorbing SO<sub>2</sub> and delaying its release into the gas phase, for explaining the behavior of high surface density TiO<sub>2</sub> coatings. The Ti<sup>4+</sup> surface sites have been proposed to act as active sites for the H<sub>2</sub>S photocatalytic oxidation, and general reaction pathways leading to the formation of SO<sub>2</sub> in the gas phase and to surface sulfates have been hypothesized, involving photogenerated holes, sulfhydryl radicals or hydroxyl radicals. The role of active sulfate radicals has been put forward for explaining the behavior turn with time on stream on sulfate-deactivated TiO<sub>2</sub>, from a progressive deactivation into a complete H<sub>2</sub>S conversion to SO<sub>2</sub>. Finally, effective regeneration treatment with recovering of the initial activity could be performed by weakly basic washing.

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### 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is a malodorous, toxic and corrosive compound, with a 0.0004 ppm low odor threshold and a characteristic rotten-egg smell [1,2], emitted from wastewater treatment or released as by-product of processes like petroleum refining, pulp and paper manufacturing. Treating H<sub>2</sub>S-containing air is important for environmental reasons (acid rain precursor contributing to global warming) and maintenance problematic (corrosive attack on process equipment), as well as for public concern over human health and comfort (noxious and nasty odor) in the frame of the indoor air quality control.

Therefore, removing H<sub>2</sub>S from air remains a relevant issue, the main actual processes being biofiltration, thermal incineration combined with catalytic processes and wet scrubbing. The works devoted to the photocatalysis degradation of H<sub>2</sub>S remained scarce by contrast to those on the mineralization of hazardous organic molecules. However, photocatalysis was reported to be efficient for removing H<sub>2</sub>S from air, with the formation of sulfates as ultimate reaction products accumulating at the catalyst surface. This causes an inherent primary problem and leads to *on-flow* deactivation [3–12]. The mechanism of the H<sub>2</sub>S photocatalytic oxidation remains not fully understood. Reaction pathways involving SO<sub>2</sub> as

oxidation intermediate [9–11] and/or the direct formation of sulfates from H<sub>2</sub>S through an eight-electron transfer process [5] have been proposed. Mechanisms involving HS<sup>•</sup> sulfhydryl radicals formed by the direct attack of H<sub>2</sub>S by holes or by reaction with OH<sup>•</sup> radicals, molecular oxygen or directly the OH<sup>•</sup> radicals have been proposed to take part in the H<sub>2</sub>S oxidation into sulfates [4–6,9–11,13]. Based on IR spectroscopy investigation, Kataoka et al. proposed that adsorbed SO<sub>2</sub><sup>–</sup> may be a possible reaction intermediate and could provide a clue as to the reaction pathway, which might help to unravel the entire eight-electron transfer process [5]. Strategies have been recently elaborated for developing low SO<sub>2</sub> selectivity photocatalytic material, *i.e.* for minimizing the release of the hazardous SO<sub>2</sub> pollutant to the gas phase and for delaying its formation in comparison to the sulfate production. It included the design of sol–gel TiO<sub>2</sub>, TiO<sub>2</sub>/M-MCM-41 (M=Cr, Ce) mesoporous systems or hybrid TiO<sub>2</sub>–SiM<sub>g</sub>O<sub>x</sub> composites for combined chemisorption and photocatalytic removal [12]. Cheap, lightweight and easily shaped UV-transparent polymeric supports for TiO<sub>2</sub> nanoparticle thin films were also studied as alternative to borosilicate glass or opaque monoliths [9].

The aim of this paper is to report on a parametric study of the H<sub>2</sub>S photocatalytic oxidation under UV-A illumination over the TiO<sub>2</sub> P25 reference, not available up to now, in terms of influence of the photocatalyst weight, the total flow rate, the relative humidity, the temperature and the UV-A irradiance. Whereas such a parametric study was already available for the photocatalytic degradation of many liquid phase pollutants such as dyes or pesticides, or of

\* Corresponding author. Tel.: +33 36885 2736; fax: +33 36885 2761.

E-mail address: [vkeller@chimie.u-strasbg.fr](mailto:vkeller@chimie.u-strasbg.fr) (V. Keller).

many gas phase hydrocarboned VOCs, no systematic results were established up to now for the H<sub>2</sub>S photocatalytic oxidation, except scarce works of Portela et al. [9,13]. Surface characterization and regeneration treatments were also investigated.

## 2. Experimental

### 2.1. Characterization techniques

Thermal gravimetry analysis (TGA) was performed using a TGA 5000 thermo-analyzer. Each sample was placed in a platinum crucible and heated from room temperature to 900 °C with a heating rate of 20 °C/min, using a 20/80 vol.%/vol.% O<sub>2</sub>/N<sub>2</sub> mixture at a flow rate of 35 mL/min.

X-ray photoelectron spectroscopy (XPS) surface characterization was performed on a ThermoVG Scientific apparatus equipped with a Al K<sub>α</sub> (1486.6 eV) source (pass energy of 20 eV). All the spectra were decomposed assuming several contributions, each of them having a Doniach–Sunjic shape [14] and a Shirley background subtraction [15]. The sulfur-to-titanium (S/Ti) surface atomic ratios have been calculated using the sensitivity factors, as determined by Scofield [16]. The subtraction of the energy shift due to electrostatic charging was determined using the contamination carbon C 1s band at 284.6 eV as reference.

Infrared Fourier transform spectroscopy (IRTF) was carried out with a Nicolet analyzer working in the transmittance mode using a 90 wt.% anhydrous KBr pellet.

The light transmission through the photocatalytic coating was directly measured on the TiO<sub>2</sub>-coated photoreactor, by comparing incident and transmitted light irradiance through the coating inside the reactor, using a wideband RPS900-W rapid portable spectroradiometer (International Light Technology).

### 2.2. Experimental device and procedure

The photocatalytic reaction was carried out in a 270 mm length single pass annular Pyrex reactor made of two coaxial tubes (*i.d.* 28 mm and *e.d.* 30 mm), between which the reactant mixture was passing through. Details concerning both reactor and device can be found elsewhere [17]. 10–800 mg of photocatalytic material, corresponding to a surface density of 0.04–3.37 mg/cm<sup>2</sup>, was evenly coated on the internal side of the 30 mm diameter external tube by evaporating a catalyst-containing aqueous suspension to dryness. The catalyst coated reactor was finally dried at 110 °C for 1 h in air.

Except for tuning the H<sub>2</sub>S and the water vapor concentrations, the composition of the reactant feed was H<sub>2</sub>S (15 ppm, corresponding to 0.023 mg of H<sub>2</sub>S per m<sup>3</sup>), air (92 vol.%), and balanced He, fed through mass-flow controllers with a total flow ranging from 100 to 980 mL/min, corresponding to total flow rates and residence times within the 0.7–6.86 cm/s and 38–3.9 s ranges, respectively. For tuning the water vapor content, the relative humidity was defined by considering 100% of relative humidity as the saturated vapor pressure of water at 25 °C and pressure of 1 atm, corresponding to about 24 Torr. A cylindrical furnace or a water-cooling system surrounding the photoreactor was used for tuning the temperature of the tests in the 22–160 °C range. The tests were mainly conducted at 500 mL/min total flow rate, with a 3.5 cm/s flow rate and a 7.6 s residence time, in dried conditions. Before the photocatalytic reaction, the catalyst was first exposed to the polluted air stream with no illumination until dark-adsorption equilibrium was reached. Afterwards the UV illumination was switched on. Illumination was provided by commercially available 8 W and 15 W blacklight tubes (Philips TL8W/08 BLB F8T5 and Sylvania T5/BL350), with a spectral peak centered around 380 nm, located inside the inner tube of the reactor. H<sub>2</sub>S and SO<sub>2</sub> were analyzed *on-line* every 3 min by a pulsed

flame photometric detector (PFPD) coupled to a CP-Sil 5 CB column on a gas chromatograph (Varian 3800).

The efficiency of the depollution process was expressed in terms of H<sub>2</sub>S conversion, of SO<sub>2</sub> selectivity – that is expected as low as possible since SO<sub>2</sub> remained a hazardous and unwanted gaseous by-product – and of sulfur removal in the gas phase, according to Eqs. (1)–(3). Depending on the test conditions, the duration at total sulfur removal could be also reported.

$$C_{\text{H}_2\text{S}}(\%) = \frac{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}}} \times 100 \quad (1)$$

$$S_{\text{SO}_2}(\%) = \frac{[\text{SO}_2]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}} \times 100 \quad (2)$$

$$\text{Sulfur removal } (\%) = \left( 1 - \frac{[\text{H}_2\text{S}]_{\text{out}} + [\text{SO}_2]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}}} \right) \times 100 \quad (3)$$

Regeneration of the photocatalysts was performed *ex situ* by washing the used photocatalysts under mechanical stirring in an aqueous or a 0.01 M NaOH solution (20 mL) at 25 °C or 50 °C for 5 h. After water washing, the samples were filtered and dried at 110 °C overnight, before being coated again inside the reactor or characterized.

## 3. Results and discussion

### 3.1. Influence of TiO<sub>2</sub> surface density

Fig. 1A–C shows the on-stream evolution of H<sub>2</sub>S conversion and SO<sub>2</sub> selectivity obtained on TiO<sub>2</sub> P25 as a function of the surface density, as well as the performances obtained after 5.5 h under stream. The influence of the surface density on both durations with no H<sub>2</sub>S release and no SO<sub>2</sub> release – this latter corresponding thus to the duration at total sulfur removal – is summarized in Fig. 2. The general behavior of the photocatalyst was characterized by an on-stream deactivation, with a quicker and more pronounced decrease in the H<sub>2</sub>S conversion for low TiO<sub>2</sub> surface densities. Increasing the surface density led to maintain a complete H<sub>2</sub>S conversion for longer durations before deactivation occurred with time on stream, and to delay the appearance of SO<sub>2</sub> in the outlet flow. The SO<sub>2</sub> selectivity seems to stabilize at a higher value with increasing density, however, at the highest surface densities tested, due to the delay in SO<sub>2</sub> appearance, the SO<sub>2</sub> selectivity was still increasing after 5.5 h of time on stream. Thus, with 15 ppm of H<sub>2</sub>S inlet concentration, both H<sub>2</sub>S conversion and SO<sub>2</sub> selectivity increased with increasing the TiO<sub>2</sub> surface density. For densities higher than 0.44 mg/cm<sup>2</sup>, the H<sub>2</sub>S conversion reached 100% and the SO<sub>2</sub> selectivity was strongly decreased. One should note that the non steady-state of both SO<sub>2</sub> selectivity and sulfur removal after 5.5 h of time on stream at the two highest TiO<sub>2</sub> surface densities, might be the reason of the observed behavior for high TiO<sub>2</sub> surface densities.

Thus, to confirm the influence of the surface density parameter, the reaction conditions have been tightened, with an increased inlet H<sub>2</sub>S concentration of 100 ppm and a total flow of 1 L/min (Fig. 3). This led to determine the optimal TiO<sub>2</sub> P25 surface density for the degradation of H<sub>2</sub>S at 2.53 mg/cm<sup>2</sup> (*i.e.* 600 mg of TiO<sub>2</sub>), with the linear increase in H<sub>2</sub>S conversion with increasing the surface density, before asymptotically stabilizing at 80%. This behavior as a function of the photocatalyst mass was in agreement with that usually reported for the photocatalytic oxidation of VOCs, with a first linear increase in the activity with the surface density, due to the increase in the amount of TiO<sub>2</sub>: this corresponds to the case for which all the particles are totally illuminated [18]. For higher catalyst amounts, a screening effect of excess particles occurs, which masks part of the photosensitive semiconductor surface, due to the limited penetration thickness of UV-A light (Fig. 4). Also, with increasing the photocatalytic coating thickness, limitation of the reactant

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