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Photocatalytic degradation and mineralization of a malodorous compound (dimethyldisulfide) using a continuous flow reactor

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Abstract

Dimethyldisulfide (DMDS) degradation and mineralization were carried out in a continuous flow reactor using TiO_2-P25 or ZnO as photocatalysts. The efficiency of the disappearance and of the mineralization of the DMDS showed to be very sensitive to the molar flow of the sulphur compounds. In our study, we have evaluated the limit average mineralization rate of DMDS per Watt emitted (for TiO_2-P25). Catalyst deactivation has been observed after several hours of complete DMDS mineralization, which was expressed by the decrease of CO_2 concentration and the appearance of residual DMDS on the outlet side of the reactor. This phenomenon is due to the inhibition of active sites on the catalyst by the formation of sulfates as final sulphur-compounds (determined by ionic chromatography). The FT-IR analysis, performed on catalyst in presence of high DMDS flow, indicated the presence of partial oxidation products such as sulfoxides, sulfones, sulfonates, sulfates and carbonyl groups. All of these disappearing after static irradiation, except for sulfate according to ionic chromatography analysis. The effect of humidity is shown; the data indicated that a detrimental effect occurs depending on the DMDS/H_2O concentration ratio. Comparison of the disappearance and of the mineralization of DMDS in presence of TiO_2-P25, commercial ZnO or home made nano-ZnO catalysts is presented and discussed. Nano-ZnO material, prepared at low temperature, showed an efficiency close to that of TiO_2-P25 while no activity was detected in the presence of commercial ZnO.

Keywords: Photocatalysis; Air treatment; Odour; Sulphur compounds

1. Introduction

Volatile organic compounds (VOCs) are commonly found in the indoor air of residences or office buildings as well as in various industrial processes, waste streams and disposal facilities. Volatile organic sulphur compounds are an important family of environmental contaminants because (i) they are characterized by a high toxicity, (ii) they are at the origin of severe corrosive attack on process equipment, (iii) their oxidation in the atmosphere results into the formation of tropospheric sulfur dioxide that can be converted into sulfuric acid (one of the main components in acid rain) [1], and (iv) due to their low odour threshold values, they contribute to odour pollution and to an olfactive nuisance. For example, the odour threshold values for methanethiol, dimethyl sulfide and dimethyl disulfide are 0.9–8.5, 0.6–40 and 0.1–3.6 ppbv, respectively [2]. These sulfur compounds are released either by natural processes such as anaerobic biological activities or by anthropogenic sources such as the Kraft paper pulping process which can lead to high local atmospheric concentrations of mercaptans. Concentration of 94 ppmv of methanethiol, 17 ppmv of DMS and 22 ppmv of DMDS were measured in gas effluents of this type of industry [3].

Conventional technologies for removing VOCs from polluted air streams involve adsorption over activated carbon, biofiltration–bioscrubbling, thermal oxidation and incineration. The latter encounters the drawbacks to be non destructive and/or expensive because of high-energy requirements and/or chemical consumption [4].

A highly promising method for the destruction of VOC is photocatalytic oxidation because it offers several advantages in

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comparison to the other processes. For example, it destroys the organic contaminants by means of a complete mineralization into carbon dioxide and water rather than transferring them from one phase to another. And it can be applied to treat a large variety of VOC's [5–7].

In addition, utilization of this process is energetically interesting because it operates at room temperature and it is possible to use solar energy to initiate the photocatalytic oxidation reactions [8]. Pioneering work on the photocatalytic destruction of H_2S and CH_3SH in a static system over a TiO_2/honeycomb support was carried out by Susuki et al. in 1991 and 1993, and it indicated no catalyst deactivation and a pseudo first order rate for methanethiol [9,10]. Some years later, Pichat et al. showed the efficiency of titanium dioxide for the destruction of some odorous compounds such as sulphur compounds [11] and Canela et al. performed a detailed study on the destruction of H_2S in humid air in a flow reactor. This latter found that the main product formed on TiO_2 surface was SO_4^{2-} which is at the origin of the deactivation only at concentrations of H_2S as high as 600 ppm [12]. Peral et al. showed that the photocatalytic degradation of dimethyl sulfide at a concentration of 100 mg/m^3 does not deactivate TiO_2 and suggested that sulfur was removed as SO_2 and/or SO_3 during the run [13]. The photocatalytic degradation of several other sulfur compounds such as trimethylene sulfide, propylene sulfide, thiophene and dimethyl disulfide in an annular photoreactor, had also been studied by Canela et al. [14] Several other works have been performed on the degradation of dimethyl sulfide in presence of TiO_2/SiO_2 [15] or in presence of TiO_2 Degussa P-25 deposited on the wall of photoreactor [16]. More recently, Vorontsov et al. realised several works on the degradation of diethyl sulfide (DES) [17–19]. They first studied the photooxidation of DES in a flow reactor over four different samples of TiO_2 and showed that the converted quantities of DES correlated well with the specific surface area of the TiO_2 samples. They also showed an enhancement of the efficiency by increasing humidity from 1 to 60% when a light intensity of 1.1 mW/cm^2 was used while an opposite effect was observed by multiplying the light intensity by a factor of 100. The two other publications deal with TiO_2 Hombikat UV 100 deposited onto the internal surface of reactor and performed a detailed study on reactivation of the photocatalyst and on the intermediate products formed in gaseous and adsorbed phase. Demeestere et al. carried out a systematic research on the effect of important process parameters like concentration, residence time, deactivation, relative humidity and a detailed study on the analysis of intermediate products and on the reactional degradation mechanism of dimethyl sulphide [20].

All the above literature's data were obtained in presence of TiO_2 in slurry or deposited on reactor but never on ZnO. However, this semiconductor material exhibits sometimes a better photodegradation performance than TiO_2 in aqueous phase. No report checked its activity for the degradation of sulphur volatile compounds and no publications try to evaluate a limit rate of mineralization of these types of sulphur compounds.

We report herein, the efficiency of several ZnO samples in DMDS degradation and a comparison of their abilities with those of TiO_2-anatase. We evaluated a limit average mineralization rate of DMDS per Watt emitted in presence of TiO_2 Degussa P-25, and studied the effect of different parameters such as DMDS concentration, total flow, humidity, and the deactivation and reactivation of the TiO_2. Finally we determined the adsorbed intermediate on photocatalyst and discussed on the reactional mechanism.

2. Experimental

2.1. Materials

DMDS was purchased from Aldrich. Titanium dioxide used was TiO_2 Degussa P-25 (anatase/rutile = 80/20; surface area = 50 m^2/g, non porous particles). Two ZnO samples were tested, a commercial sample provided by Aldrich ($ZnO_{(AL)}$) and a home made sample prepared at low temperature from $Zn[N(SiMe_3)_2]_2$ [21] which was calcinated at 700 °C ($ZnO_{(700)}$) or not ($ZnO_{(NC)}$). The procedure used for their preparation is described in detail in the publication of Daniele et al. [22]. 1.54 g of $Zn[N(SiMe_3)_2]_2$ in 4 mL of hexane were added dropwise to 50 mL of water under vigorous stirring. The mixture was stirred for 2 h and then centrifuged to give a white solid. The as-prepared solid was washed by 50 mL of ethanol and dried at 70 °C for ca. 12 h. The powder obtained is denoted $ZnO_{(NC)}$, its surface area was equal to 56 m^2/g with a total pore volume of 0.192 cm^3/g, after annealing at 700 °C the surface area dropped to 13 m^2/g.

2.2. Photoreactor and light source

Photocatalyic tests were performed in a dynamic microreactor of about 100 mL equipped with an optical window made of Pyrex glass (transmittance: wavelength >290 nm) a high pressure mercury lamp (Philips HPK 125 W), emitting 7.5 mW/cm^2 at 365 nm, a water cell used to remove IR beams and to avoid heating and a Whatman filter (10 cm^2 of diameter) where the powder of photocatalyst (20 mg (for TiO_2) or 40 mg (for ZnO)) is deposited. The experimental apparatus is illustrated in Fig. 1.

The distance between the lamp and the photocatalyst is 72 mm. Radiant flux was measured by using a Bioblock Scientific model CX-365 radiometer.

Gaseous DMDS with high purity clean air ($N_2:O_2 = 8:2$; water concentration <3 ppm) was fed through the photocatalyst by mixing the vapor pressure of VOC using a saturator maintained by a cryostat at the desired temperature. Water vapor was obtained by passing dried air through a tube containing deionised water, at the desired temperature. Before the gas stream containing the VOCs was introduced into the photoreactor, oxygen was passed through the illuminated photoreactor for 24 h to preatreat the catalyst. The UV irradiation experiments were started after the inlet and outlet DMDS concentration were equal. The conversion of VOCs and

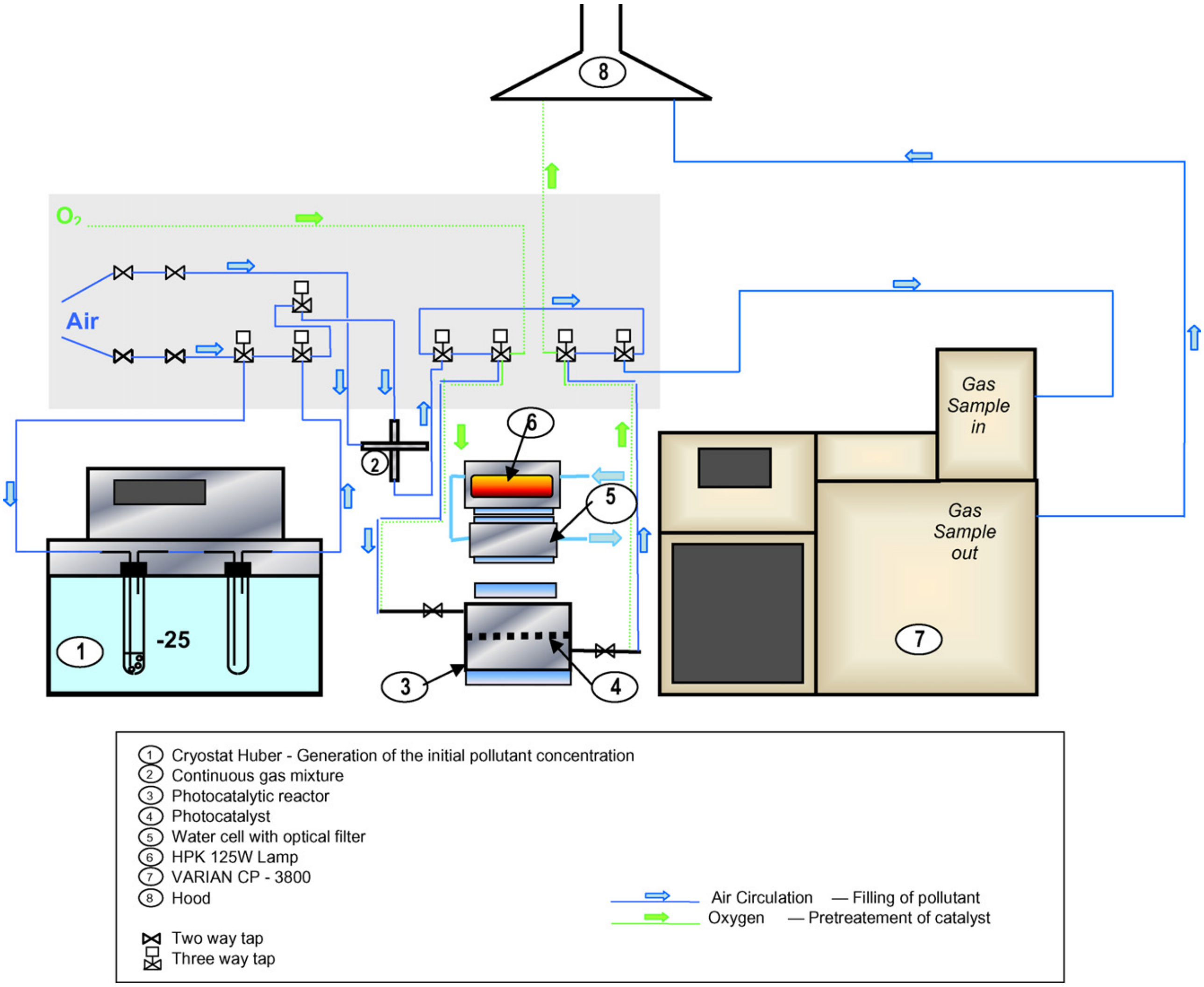

Fig. 1. Dynamic photocatalytic set-up.

yields of decomposition products were calculated from the following equations:

$$\text{conversion of DMDS}\,(\%) = \frac{[\text{DMDS}]_{\text{inlet}} - [\text{DMDS}]_{\text{outlet}}}{[\text{DMDS}]_{\text{inlet}}} \times 100, \qquad \text{CO}_2\,(\%) = \frac{[\text{CO}_2]_{\text{outlet}}}{2 \times [\text{DMDS}]_{\text{inlet}}} \times 100$$

2.3. Analyses

The evolution of DMDS and of the CO_2 was followed using a VARIAN 3800 chromatograph equipped with a VARIAN Pulsed Flame Photometry Detector (PFPD) and a VARIAN Thermic Conductibility Detector (TCD) respectively. Three columns were used, a Hayesep T 0.5 m × 1/8 in. Ni 80/100 CP81072 to determine CO_2, a Molsieve-13 X 1.5 m × 1/8 in. SS 80/100 CP81071 to measure CO, CH_4, O_2, N_2 and a CP-Sil 50 m × 0.32 mm (5.0 μm) FS CP7690 placed in parallel to these two former columns. This latter column allows analysing DMDS and other sulfur organic compounds.

For the identification of acid and sulfate adsorbed on the TiO_2 surface, solid–liquid extraction was performed. TiO_2 was suspended and stirred for 1 h in deionised water adjusted at pH 8 with NaOH. After filtration, the sample in a vial was taken by an autosampler. The analyses of organic acid compounds were performed by HPLC with a Sarasep column (length: 30 cm; inner diameter: 7.8 mm) and a Varian detector at 210 nm. The mobile phase was H_2SO_4 5×10^{-3} M and the flow rate 0.7 ml/min. The formation of sulfate ions and methane sulfonic acid was followed by ionic chromatography using a Dionex DX-120 pump, a conductivity detector, and an IonPac AS14A (250 mm × 4 mm) column. The flow rate was 1 mL/min; the mobile phase was 8 mmol/L Na_2CO_3 and 1 mmol/L $NaHCO_3$.

FT-IR experiments were performed by ATR using a Perkin-Elmer spectrum one spectrophotometer.

Percentage of absorbed light (%Abs) was determined by measuring the radiant flux (A) over different amounts of photocatalyst and comparison to the radiant flux measured without photocatalyst (A_0) by using the following expression:

$$\%\mathrm{Abs} = \frac{A_0 - A}{A_0}$$

3. Results and discussion

3.1. Efficiency of TiO_2 and ZnO

TiO_2 is the main semiconductor used in the photocatalytic field due to its high efficiency and good chemical and thermal stability. ZnO presents a band-gap close to that of TiO_2 [23] and is more efficient than TiO_2 to produce H_2O_2. Kormann et al. have found a quantum yield for the initial formation of hydrogen peroxide of 15% on ZnO and only 1% on TiO_2 [24]. However, in aqueous phase ZnO is not stable and Zn^{2+}, a toxic cation, is formed. This drawback limits its use in the photocatalytic treatment of water. In gas phase, this photocatalyst is stable but is little studied [25] and is frequently employed to avoid the poisoning of catalyst by sulfur compounds in hydrotreatment [26]. These important adsorption properties of sulfur compounds and its particular properties to form hydrogen peroxide lead us to test and compare its photocatalytic efficiency, in the DMDS gas phase degradation, with those of TiO_2 Degussa P-25, the photocatalyst used as reference in the photocatalytic field.

Two ZnO samples were tested, a commercial sample provided by Aldrich ($ZnO_{(AL)}$) and a home made sample prepared at low temperature from $Zn[N(SiMe_3)_2]_2$ [22] which was calcinated at 700 °C ($ZnO_{(700)}$) or not ($ZnO_{(NC)}$). No efficiency of $ZnO_{(AL)}$ or of $ZnO_{(700)}$, was observed while about 40% of DMDS disappeared at the pseudo steady state, from which 15% of DMDS is mineralized into CO_2 for the $ZnO_{(NC)}$ sample.

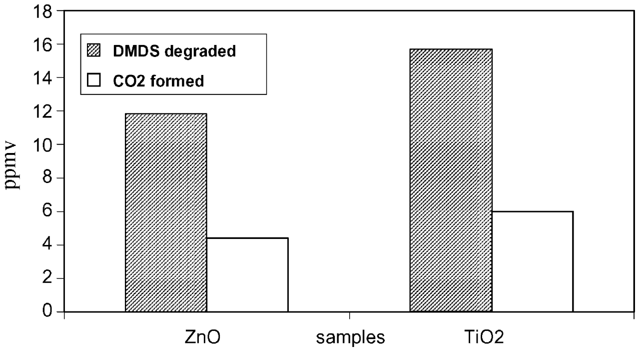

Fig. 2. Comparison of ZnO_{NC} and TiO_2 Degussa P-25 efficiency in the disappearance and mineralization of DMDS. ([DMDS] = 30 ppm; $[H_2O] < 3$ ppm).

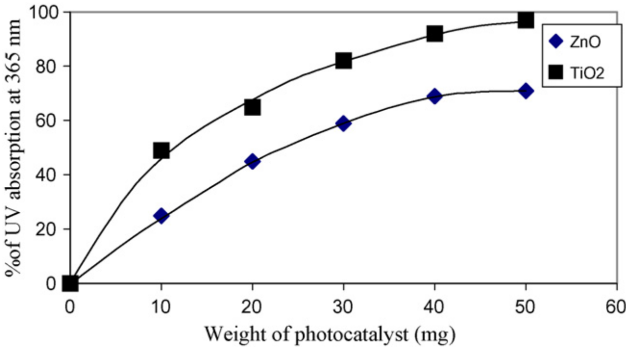

Fig. 3. Comparison of UV absorption of TiO_2 and ZnO_{NC} at 365 nm as a function of photocatalyst weight.

Fig. 2 compares the disappearance and the mineralization of DMDS in presence of home made ZnO samples named $ZnO_{(NC)}$ and TiO_2 Degussa P-25. TiO_2 P-25 presents a amount of DMDS degraded only about 25% higher than that of ZnO_{NC} and a percentage of mineralization into CO_2 of 20 and 13% respectively, in both cases (under our experimental conditions, indicated the presence of organic intermediates compounds either adsorbed or present in gaz phase. According to the FT-IR analysis of TiO_2 surface performed after 24 h of irradiation, several organic compounds were adsorbed on photocatalyst as discussed in Section 3.5. Moreover, it was also observed the formation of a VOC in gas phase in the presence of TiO_2 Degussa P-25 while no VOC are detected in the presence of ZnO probably due to their adsorption on the photocatalyst surface.

The nature of ZnO plays an important role. The calcinated sample or commercial one are totally inactive whereas it is noteworthy that ZnO displays efficiencies in the disappearance and the mineralization of DMDS only 25–30% smaller than TiO_2 P-25 ones. Commercial (ZnO_{AL}) and 700 °C calcinated materials (ZnO_{700}) behaved as if their surface was rapidly poisoned under a dynamic flow of DMDS while as-prepared ZnO acted as a promising material for removal of disulfides compounds. The reason for the different efficiencies of the various ZnO photocatalysts appears to be correlated to the specific area values. Actually, ZnO_{AL} and ZnO_{700} have a very small surface area compare to ZnO_{NC}. The as-prepared ZnO (ZnO_{NC}) exhibits the same surface area (56 m^2/g) than the TiO_2-P25 Degussa (50 m^2/g). However the percentage of UV absorbed at 365 nm is slightly smaller for ZnO_{NC} compared toTiO_2 Degussa P-25 (Fig. 3).

While 100% of light was absorbed by 40 mg of TiO_2 only 70% was absorbed by ZnO, suggesting the formation of lesser amounts of reactive species in the same experimental

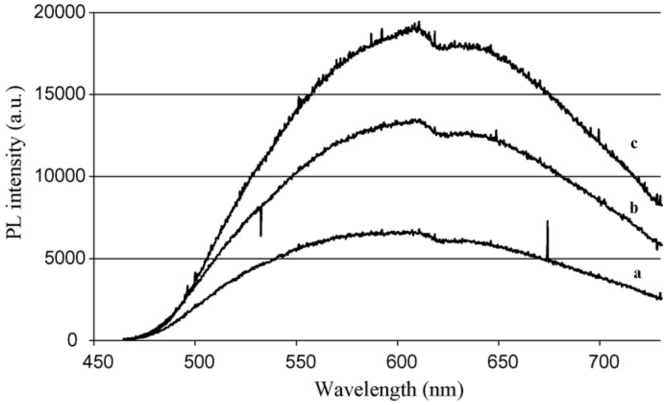

Fig. 4. Photoluminescence spectra of as-prepared ZnO (a) without DMDS, (b) in DMDS atmosphere and (c) in DMDS atmosphere + irradiation at 355 nm for 30 min.

conditions. This difference of light absorption could be at the origin of the slightly smaller efficiency of ZnO_{NC} compared to that of TiO_2 Degussa P-25.

Photoluminescence measurements of nano-ZnO particles showed a substantial enhancement (twice) of the green emission intensity when it was performed under DMDS atmosphere (Fig. 4). This enhancement can be increased by carrying out photoluminescence measurements after irradiation at 355 nm for 30 min. Since the green luminescence intensity is dependent of the numbers of singly ionized oxygen vacancies [27], it can be suggested that their numbers are much more than in nano-ZnO particles without DMDS and that in the photocatalytic process, oxidative degradation consumes oxygen onto the ZnO surface, increasing oxygen vacancy amounts. However, further experiments are necessary to establish a detailed reaction mechanism for the oxidative decomposition of DMDS.

3.2. Effect of total flow rate and of initial DMDS concentration

The effect of flow rate on the mineralization of DMDS was investigated and it is represented on Fig. 5. The effect was examinated at an initial concentration of 77 ppmv. The results indicate that by increasing the flow rate until about 1.3 L/min the total mineralization of DMDS is achieved. This implies that all DMDS molecules reach the photocatalyst surface at a flow rate in this range and mass transfer limitations are not observed. From a total flow of 1.3 L/min, the conversion dropped as the flow rate was increased. Several authors reported this same behavior in presence of a thin film of TiO_2 deposited on the photoreactor and attributed the decrease of conversion to a mass transfer problem [17,28]. In our experimental conditions (i) the pollutant flow went through the photocatalyst and (ii) it has been checked that at the same molar flow, varying total flow and initial DMDS concentration, the percentage of mineralization was similar. So, we suggest that the gradual decrease of conversion from 1.3 L/h was due to the reduction of contact time.

If we define the disappearance rate as: $r = (C_{\text{in}} - C_{\text{out}}) \times Q$, where C_{in} and C_{out} are the inlet and the outlet contaminant concentration respectively and Q is the total flow, a total DMDS mineralisation can be achieved until a DMDS flow rate of about 4.2 μmol/h is reached.

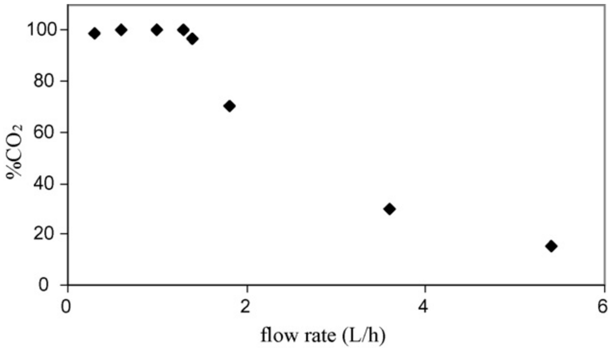

Fig. 5. Mineralization percentage vs. flow rate. [[DMDS] = 77 ppm; m_{TiO_2} = 20 mg; $[H_2O] < 3$ ppm)].

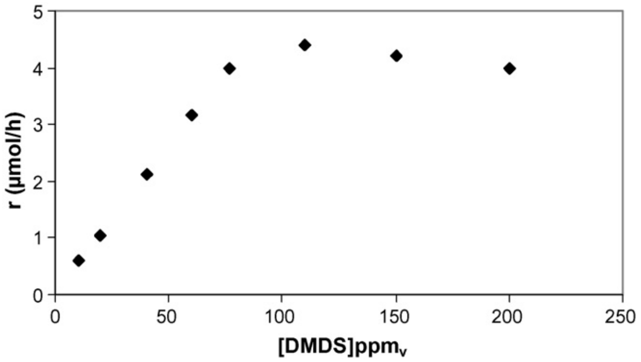

Fig. 6. Disappearance rate of DMDS vs. the initial inlet concentration (flow rate = 1.3 L/h; m_{TiO_2} = 20 mg; $[H_2O] < 3$ ppm).

The mineralization rate for DMDS *versus* the inlet concentration (10–200 ppmv) under a flow rate of 1.3 L/h is shown in Fig. 6. The reaction exhibits a pseudo-first-order dependence on DMDS concentration within the range of the concentrations used (until about 77 ppmv), then the mineralization of DMDS drops slowly when the feeding concentration increases probably due to the poisoning of the TiO_2 surface.

From these results we can determine the maximal DMDS flow rate, which can be totally mineralized by the UV radiant flux, considering that all photons are absorbed and it corresponds to about 14 μmol/(h W) which is in agreement with the value mentioned in literature for other VOC [30].

3.3. Photocatalyst deactivation and regeneration

A detailed investigation of the catalyst life and its possible deactivation was carried out by monitoring the disappearance and the mineralization of DMDS over a long experiment (>24 h) under a continuous flow of 3 L/h of DMDS at a concentration of 80 ppmv using less than 3 ppm of water. The results are summarized in Fig. 7. As can be noted, the percentage of DMDS disappearance dropped from about 90–70% after 20 h of irradiation, simultaneously the concentration of CO_2 decreased

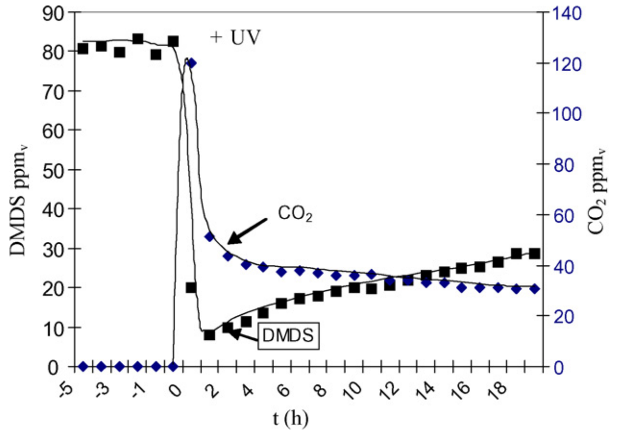

Fig. 7. Evolution of DMDS and CO_2 concentration as a function of time to visualize the deactivation of catalyst. ([DMDS] = 80 ppm; flow rate = 3 L/h; m_{TiO_2} = 20 mg; $[H_2O] < 3$ ppm).

also. This decrease in the photocatalytic efficiency of TiO_2 could be due to the adsorption of by-products of the oxidation of DMDS. This hypothesis is related to the fact that (i) organic surface species and (ii) sulfate ions were detected by FT-IR analysis of TiO2 photocatalyst taken after 24 h of irradiation (see Section 3.5). Confirmation that sulfate ions are the major product generated during the photocatalytic destruction of DMDS was obtained by washing the TiO_2 photocatalyst with water and determining the amount of sulfate in this supernatant. The mass balance showed that 70% of the total disulfide that entered in the reactor was recovered as sulfate. The other 30% could correspond to the organic sulphur compounds formed during the experiment as seen by FT-IR.

After deactivation of the photocatalyst, three types of regeneration procedures have been tested. The first reactivation procedure consisted of passing humidified air through the illuminated photocatalyst until all adsorbed organic compounds were oxidized. The total mineralization of the organic intermediates was monitored by measuring the CO_2 concentration. After this first reactivation procedure, only about 30% of the efficiency was recovered. The second reactivation procedure consisted of completing the first procedure by washing the photocatalyst with water. The FT-IR analysis of TiO_2 photocatalyst after these two procedures showed the presence of residual sulfate (around 1154 and 1040 cm^{-1}) suggesting the presence of sulfate, strongly attached to the catalyst and not desorbed by washing with water. In these conditions more than 80% of photocatalyst efficiency was recovered.

It is also interesting to note that the deactivation seems to be more important and begins earlier, using a humidity level of 50%, corresponding to 12,300 ppm of water in our conditions. This behavior could be explained by the formation of a higher amount of sulfate adsorbed on TiO_2 as mentioned by Vorontsov [17]. In the absence of water, sulfur atoms could partially transformed into SO_2. However, in our experimental conditions, no SO_2 has been observed.

The last procedure of regeneration consisted of passing humidified air through the illuminated photocatalyst followed by washing TiO_2 with an alkaline water solution at pH 8 and then rinsing with water. After this latest generation procedure, no organic compound or sulfate were detected and the initial efficiency of the catalyst was recovered. In literature, Vorontsov et al. tested also different reactivation procedures, one is the use of a humidified air flow through the illuminated photocatalyst until all adsorbed organic compounds were oxidized, the other procedure is the rinsing of the catalyst with water [17] and showed that rinsing is a necessary step of the reactivation procedure because it allows to remove SO_4^{2-} adsorbed. However, these authors never suggested a washing at alkaline pH to favorise the desorption of sulfate and the catalyst was extensively washed with water for 5 days to totally remove SO_4^{2-}.

3.4. Air humidity effect

Experiments were carried out using different concentrations of water in a range from less than 3 to 24,000 ppm and a fixed concentration of DMDS to 77 ppmv. The percentage of DMDS degraded and mineralized into CO_2 is represented as a function of water concentration in Fig. 8.

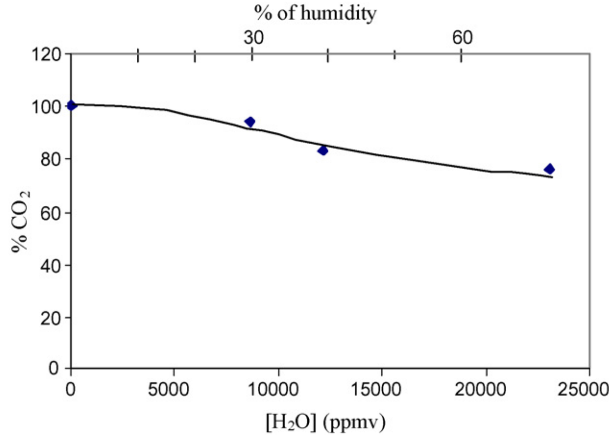

Fig. 8. Percentage of DMDS mineralization *vs.* humidity. [[DMDS] = 77 ppm; flow rate = 0.8 L/h; m_{TiO_2} = 20 mg].

In our experimental conditions, the efficiency of TiO_2 was significantly lower when the humidity increased. At high water concentration, the reaction rate was slightly decreased due to a competition of adsorption with water molecules [31–33]. As a matter of fact, water can physisorb on the surface hydroxyl groups via hydrogen bonding as shown by Gregg et al. [34] and Raupp et al. [35] and be in competition with DMDS adsorption. It is also interesting to note that by increasing the concentration of DMDS to 115 ppmv, no inhibition occurs using 23,000 ppmv of water. This behavior is in agreement with a competition on the adsorption of water and of contaminant on TiO_2 surface area.

This result differs from those observed in the degradation of diethyl sulfide by Vorontsov et al., who found that moderate humidity increases conversion compared to dry air [18] and from other authors, on different type of contaminants, whose an increasing of the efficiency at low relative humidity was observed [20,31–33,36–38]. This discrepancy was probably due to the ratio between the concentration of contaminant and of water molecules used in these different experiments. Actually, Obee et al. [36] showed that the location of the maximum of efficiency depends on the contaminant and humidity levels and that it shifts to higher humidity as contaminant concentration is increased as predicted by a bimolecular Langmuir–Hinshelwood form.

The important mineralization of DMDS in dry air, [water] < 3 ppmv, suggests that due to its ionization potential DMDS can react directly to form a cation-radical $DMDS^{\bullet+}$ which can react with $O_2^{\bullet-}$ to give RR′S=O; $RR'SO_2$ and RSO_3^{-}. This type of reaction has already been suggested by Demeestere et al. [20].

3.5. Reaction products and degradation pathways

During the photocatalytic degradation experiments carried out at a flow rate of 1.3 L/min and a [DMDS] = 150 ppm in a dry air, reaction products accumulated on the photocatalyst

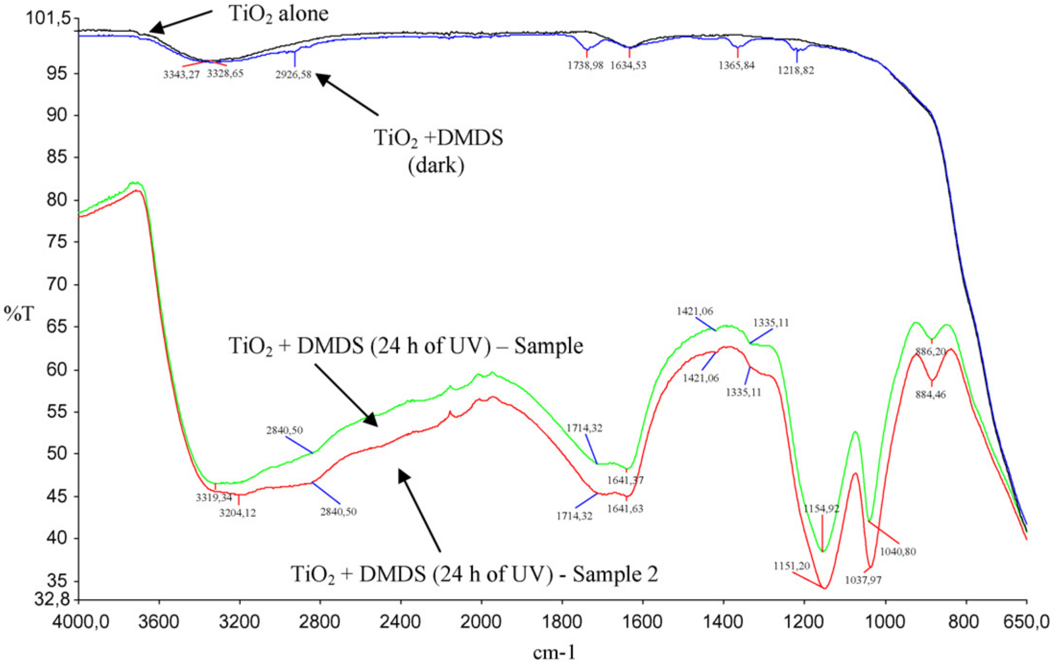

Fig. 9. IR analysis of pure TiO_2, TiO_2 after adsorption of DMDS and TiO_2 + DMDS after irradiation during 24 h (two samples were analysed to check the reproducibility). ([DMDS] = 150 ppm; flow rate = 1.3 L/h; m_{TiO_2} = 20 mg; [H_2O] < 3 ppm).

surface were analysed by FT-IR and ionic and reverse phase chromatography. Simultaneously, reaction products released in the gas-phase were determined by direct analysis using TCD and PFPD detectors.

In gas phase, only two products were detected with our experimental conditions, CO_2 and a volatile sulphur compound non identified. Ionic chromatography analysis of an alkaline aqueous (pH 8) extract of TiO_2 showed the presence of sulfate and methanesulfonic acid. The concentration of sulfate detected on TiO_2 corresponds to about 70% of DMDS converted. Reversed phase chromatography analysis for the same extract revealed the presence of formic acid.

Infrared studies were carried out to investigate the formation of by-products on the TiO_2 surface without extraction. FT-IR spectra of (a) pure TiO_2, (b) TiO_2 after DMDS adsorption during 24 h and (c) irradiated TiO_2/DMDS are shown in Fig. 9.

Infrared spectrum of pure TiO_2 (a) shows strong absorption bands at 3334 and 1634 cm^{-1}, which is typical of adsorbed water on TiO_2, as already reported in the literature [12]

After exposing the catalyst to DMDS for 24 h in the dark (b), very small bands situated at 2926, 1738, 1365 and 1218 cm^{-1} are present. Bands at 2926 and 1365 cm^{-1} are characteristic of CH_3 and CH_3–S, while those at 1738 and 1218 cm^{-1} are not due to DMDS but probably to impurities.

After 24 h of irradiation, Fig. 9 reveals the presence of large IR band in the range 3600–3000 and 1700–1600 cm^{-1} characteristics of the presence of water, indicating that H_2O was formed during the photocatalytic degradation of DMDS and remained adsorbed on TiO_2 surface. The appearance of two new important bands at 1037 and 1151 cm^{-1} with a shoulder and two smaller one in the range 1420–1300 cm^{-1} characteristics of the asymmetric and symmetric S=O stretching frequency ranges for sulfonates, sulfates and sulfonic acids [39] confirm the formation of sulfate and methanesulfonate detected by ionic chromatography. Band near 1714 cm^{-1}, and in the range 2900–2800 cm^{-1} showed also the presence of C=O and methyl groups.

To summarize, several organic intermediates were detected in the degradation of DMDS showing the presence of different types of reaction: (1) oxidation of sulphur, (2) oxidation of carbon and (3) breaking of S–S bond. The most important is the formation of sulfate ions, which represent about 70% of DMDS converted.

From these results, it is difficult to determine if DMDS is directly oxidized by hole (DMDS + $h^+ \rightarrow DMDS^{\bullet +}$) or by the hydroxyl radical formed by the reaction with hole and H_2O in situ generated. Actually, Hatakeyama et al. [29] have shown that DMDS reacts with OH radical via addition (to afford $CH_3S(OH)SCH_3$) followed by rapid cleavage of the S–S bond to form HCHO + SO_2 or MSA as final products. However, at the beginning of the experiment because water is not present (using of dry air), direct oxidation could be the most important relational pathway. Both reactional mechanisms were also proposed by Demesestere et al. [20] in the photocatalytic degradation of dimethyl sulfide.

4. Conclusions

The study provided data on (1) the efficiency and (2) the relational mechanism of photocatalytic gaseous dimethyldisulfide (DMDS) degradation onto UV irradiated TiO_2 Degussa P-25, in comparison with those of three ZnO samples. First, it was found that the ZnO sample efficiency was strongly dependant of its surface area and could display similar efficiency than TiO_2 Degussa P-25. Photoluminescence measurements suggest that oxygen of ZnO lattice participated to oxidation process. The study of the effect of initial concentration, total flow and air humidity allowed us (1) to evaluate a limit average mineralization rate of DMDS equal to about 14 μmol/L/W, (2) to show that humidity slightly inhibited mineralization at high concentration due to the adsorption competition between DMDS and H_2O and suggests that, initially, DMDS reacts with h^+ to form DMDS+ radical which is oxidized by $O_2^{\bullet -}$. Concerning the lifetime of photocatalyst, it was determined that the deactivation was mainly due to the formation of sulphate at low DMDS concentration and also to the accumulation of organic molecules at higher concentration of DMDS.

FT-IR spectra of irradiated TiO_2 and chromatographic analyses of solid–liquid extraction product revealed the presence of formic acid, methane sulfonic acid and sulphate which can be totally mineralized after a longer irradiation, except for the sulfate which is at the origin of the deactivation of the photocatalyst. This latter could be totally removed by washing TiO_2 with an alkaline aqueous solution. Then, a protocol of total photocatalyst regeneration has been established consisting of passing humidified air through the illuminated photocatalyst followed by washing TiO_2 with a basic aqueous solution.

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