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Photocatalytic-based strategies for H_2S elimination

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ABSTRACT

The mechanism of H_2S elimination in gas phase by means of heterogeneous photocatalysis was investigated. The main drawbacks for a real application were identified to be related to the nature of the reaction products: SO_2 is toxic, corrosive and malodorous, and $SO_4{}^{2-}$ accumulates on the photocatalyst surface leading to deactivation. In order to face this challenge, supported photocatalysts with different properties were synthesised to investigate several strategies according to the photocatalyst selectivity. On one hand, two different approaches for coupling adsorption and photocatalysis have been proposed to solve the problem of SO_2 release and prolong the catalyst lifetime. First, porous and SO_2-selective photocatalysts were synthesised by sol–gel with the help of surfactants. These materials presented good conversion values and suffered slower deactivation; an external adsorption unit might retain the SO_2 produced. Alternatively, improved adsorption capability of the photocatalyst was obtained through the synthesis of coated and incorporated hybrid TiO_2–SiMgOx composites, whereby SO_2 release was avoided and the lifetime of the photocatalyst prolonged. The combination in a hybrid material of an efficient photocatalyst and an adsorbent that may act as support constitutes a promising alternative for H_2S elimination due to the coupling of photocatalytic and adsorptive properties. On the other hand, photocatalyst regeneration was achieved by rising with water, which recovered the active sites. Moreover, when a 1 M KOH solution was used in the process, the creation of new basic active sites resulted in an increase of the photocatalytic activity, even higher than for the fresh material.

1. Introduction

Hydrogen sulphide is a toxic and corrosive compound released into the atmosphere in many industrial processes [1]. Wastewater treatment, sour gas flaring, petroleum refinery and pulp and paper production are some of them. Especially important is the case of wastewater treatment facilities, where fatal episodes can occur during maintenance routines [2]. In water pretreatment areas H_2S concentration is between 5 and 15 ppm, reaching values of 60–80 ppm or even higher in anaerobic digesters. H_2S presents a TLV-STEL value of 10 ppm and an odour threshold of 0.5 ppb [3]. For these reasons H_2S removal is a target of interest. Conventional methods commonly used to control the emissions of this compound include biofiltration, chemical scrubbing, incineration or adsorption technologies [4–6]. These methods lack long-term stability, are non destructive or require chemicals or high energy consumption.

Photocatalysis is an advanced oxidation process (AOP) where the photogeneration of electron hole pairs promotes both oxidation and reduction reactions. This technology is widely applied to the oxidation of volatile organic compounds (VOCs) [7] and has the potential to be a promising method for removing H_2S, but very little can be found in the literature about this subject. Canela et al. and Kato et al. have proposed the complete oxidation of H_2S to sulphate through the following mechanism, where electrons and holes are trapped by adsorbed water, superficial OH^- and O_2 [8,9]:

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

$$h^+ + H_2O_{ads} \rightarrow OH^{\bullet} + H^+ \quad (2)$$

$$h^+ + OH^-_{superf} \rightarrow OH^{\bullet} \quad (3)$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (4)$$

$$H_2S + 8OH^{\bullet} \rightarrow SO_4^{2-} + 2H^+ + 4H_2O \quad (5)$$

$$H_2S + 4H_2O_2 \rightarrow SO_4^{2-} + 2H^+ + 4H_2O \quad (6)$$

Sulphate formation poses an inherent primary problem. It has been reported that sulphate accumulates on the catalysts surface, covering the active sites and leading to a progressive catalyst

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deactivation. Moreover, in previous works the formation of SO_2 as gaseous reaction product has been reported [10–12]. As in the case of H_2S, this compound is toxic, corrosive and malodorous, and therefore should be avoided. Considering these points, it is necessary to study how to improve the photocatalyst lifetime and avoid or retard the formation of non-desirable products.

TiO_2 is the most widespread semiconductor used in photocatalytic applications. This oxide shows the best balance of efficiency, chemical stability, low toxicity and price. For gas phase applications supporting this material is a requirement, in order to avoid the release of fine particles into the atmosphere or expensive filtration processes. Among the wet chemical routes, sol–gel is an effective, versatile and the most commonly used method to prepare immobilized TiO_2 thin films. Properties such as particle size, morphology, crystal phases and textural properties can be modulated by variations of the synthesis method [13]. Therefore, it is possible to tailor the photocatalytic properties of the semiconductor, for example by promoting the formation of porous structures. The higher photocatalytic performance of porous TiO_2 films has been reported by several authors [14–16].

An attractive alternative for photocatalysts synthesis consists in the development of hybrid composites, where the combination of adsorption and photocatalytic properties induces a synergism towards abatement of pollutants [17–20]. The overall abatement process will thus be of dual nature. These materials may attenuate the variations in the concentrations of pollutant agents, enhance the photocatalytic efficiency and retard/avoid by-products desorption, as well as mitigate the problem of long-term stability of pure adsorbents. An interesting and inexpensive base material for these composites is SiMgOx. It is used as adsorbent [21] due to its high surface area and porosity [22,23], and recently it has been used as support of organic sensitizers in heterogeneous photocatalysis as well [24].

Thus, in this work several strategies have been investigated in order to solve the problems posed by H_2S photocatalytic reaction products: first, the synthesis of photocatalysts that favour the sulphate formation, and their regeneration through non aggressive methods to recover the active sites; second, the development of highly SO_2-selective photocatalysts with slow deactivation; finally, the improvement of the adsorption capability of the photocatalyst through hybrid composites, which might avoid SO_2 release into the environment and/or prolong the life of the photocatalyst.

2. Materials and methods

Different commercial and synthesized TiO_2, alone or as part of TiO_2–SiMgOx hybrid materials, were prepared using different synthesis routes The photocatalytic activity was evaluated supporting the oxides on glass plates in order to minimise the physical differences between them. Below, the main characteristic of each synthesis route are briefly described.

2.1. Preparation of TiO_2 coatings: sol–gel route A

This sol–gel procedure A is described in detail elsewhere [11,25]. Briefly, the sols were prepared by addition of titanium isopropoxide (TISP; Aldrich) to an aqueous solution of nitric acid in the proportion 900:6.5:74 (H_2O:HNO_3:TISP). Subsequently, the suspensions were stirred for about 24 h until peptization was completed. The acidic sols were dialyzed to a final pH of 3.4. The TiO_2 was deposited on glass-slides (30 mm × 90 mm) or rings (L = 13.7 mm, d_{ext} = 4 mm, d_{int} = 2 mm) by a dip-coating procedure, submerging the supports into the sol and withdrawing them at a rate of 0.8 mm s^{-1}. This process was repeated five times in order to achieve the desired TiO_2 loading. After applying each layer, the plates were dried in air at 100 °C for 1 h. Finally, the samples were fired at 350 °C for 2 h at a heating rate of 10 °C min^{-1}. These samples are identified as TiO_2-A.

2.2. Preparation of TiO_2 coatings: sol–gel route B

Titania sols B were prepared using titanium isopropoxide as precursor via acid catalysis. TISP was chemically modified with acetyl–acetone (AcAc) or acetic acid (AcOH) using a molar ratio TISP/complexant = 1, to control hydrolysis and condensation reactions. Non ionic surfactants, Pluronic F-127 or polyethylene glycol hexadecyl ether P5884 Brij58, provided by Sigma–Aldrich, were incorporated to the sol using a molar ratio surfactant/TISP = 5×10^{-4} and 7×10^{-2}, respectively. In the case of the sols prepared with F-127, acetyl–acetone was selected as complex agent, since acetic acid produced the destabilization of the sol. For sols prepared with Brij58, AcOH was used, according to preliminary tests where it showed better photocatalytic activity. Finally, a mix of ethanol and acidified water (0.1 M HCl) was added drop wise into the solutions. A reference sol with AcOH was prepared following the same route but without surfactant addition.

TiO_2 films were deposited on glass-slides (30 mm × 60 mm) by dip-coating at a withdrawal rate of 25 cm min^{-1} for the reference sol and 35 cm min^{-1} for the sols with surfactant. All coatings were treated at 450 °C for 1 h using a heating ramp of 10 °C min^{-1}. The glass-slides were coated with a first layer of SiO_2 [26,27] (200 nm) to avoid the diffusion of Na^+ cations from the glass substrate to the TiO_2 coating during the firing. These samples are named TiO_2-F127, TiO_2-Brij58 and TiO_2-dense.

Additionally, W and Ca doped samples were prepared incorporating 0.5% molar of tungsten (II) dichloride (WCl_2) and 3% molar of calcium nitrate ($Ca(NO_3)_2$) to sols B prepared with Brij58.

2.3. Preparation of hybrid materials

In order to synthesise hybrid photocatalysts, first flat plates with adsorption properties were prepared by extrusion. The doughs were obtained kneading a mixture of TiO_2-anatase (G-5, Millenium) and SiMgOx (sepiolite, Tolsa S.A.) or pure SiMgOx with water [19,20]. The optimum TiO_2 to SiMgOx ratio selected to carry out this study was 1:1, since this proportion combines good textural and mechanical properties [23]. The plate-shaped materials were dried at room temperature for 48 h, then at 150 °C for 12 h and finally treated at 500 °C for 4 h in air to obtain the desired crystalline phases. The resulting plates had the following dimensions: wall thickness 2 mm, geometric surface 19.76 cm^2 (2.6 cm × 7.6 cm).

To evaluate their photocatalytic activity in operating conditions close to those of TiO_2 thin films and to minimise the masking effect of their high adsorption capacity, the plate-shaped materials were crushed and suspended in 2-propanol; this suspension was used to coat glass plates with a thin layer of material. Finally, the samples were dried at 100 °C. Three samples were prepared following this procedure: one of TiO_2–SiMgOx, containing 20 mg of TiO_2 (TiO_2–SiMgOx incorporated sample) and two of SiMgOx. A suspension of P25 TiO_2 from Degussa in 2-propanol was prepared to coat one of the SiMgOx samples with 20 mg of TiO_2 to obtain the TiO_2–SiMgOx coated sample.

For the adsorption study similar TiO_2–SiMgOx ceramic plates with 1 mm wall thickness were extruded. After calcination at 500 °C for 4 h in air, the plates were gently crushed and sieved. The fraction in between 2 and 4 mm was taken out and used for conventional H_2S dynamic adsorption studies.

2.4. Photocatalytic activity measurements

The glass plates were placed in a continuous-flow flat photoreactor with a top borosilicate glass window irradiated with

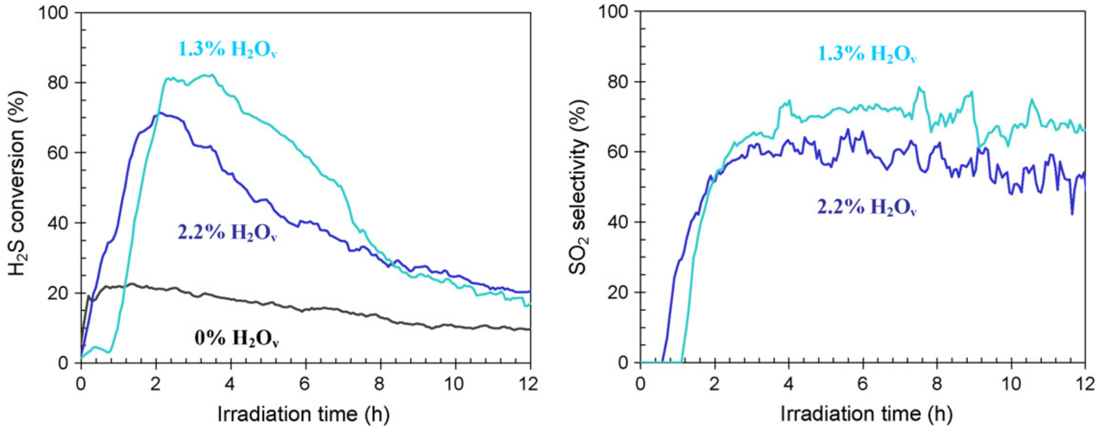

Fig. 1. Photocatalytic activity of TiO_2-A samples at different water vapour contents: H_2S conversion (left) and selectivity towards formation of gaseous SO_2 (right). During the test at 0% H_2O_v hydrogen sulphide degradation was not high enough to quantify the SO_2 formation.

4.4 mW cm^{-2} by two 8-W UV-A lamps (Philips, maximum emission at 365 nm) to analyse the performance of the different synthesised materials. H_2S in N_2 was supplied by L'Air Liquide and diluted with wet or dry air. The experiments were usually conducted at 75 mL min^{-1} total gas flow, 15 ppm H_2S, 1.3% water content and a residence time of 3.6 s.

The composition of the gas stream was analysed by a Varian CP4900 micro-GC equipped with a microthermal conductivity detector. The irradiation run started when the stationary state in the dark was reached. H_2S conversion and selectivity to SO_2 were calculated according to Eqs. (7) and (8):

$$X_{H_2S} = \frac{[H_2S]_{inlet} - [H_2S]_{outlet}}{[H_2S]_{inlet}} \times 100 \quad (7)$$

$$S_{SO_2} = \frac{[SO_2]_{outlet}}{[H_2S]_{inlet} - [H_2S]_{outlet}} \times 100 \quad (8)$$

Once the samples were deactivated, the photocatalysts were washed and the composition of the solution was analysed by ionic chromatography with a DIONEX DX-500 equipped with a conductivity detector.

2.5. Conventional H_2S adsorption measurements

For evaluation of the adsorption capacity of the hybrid TiO_2–SiMgOx composite the fraction of material with sizes between 2 and 4 mm was transferred into a cylindrical reactor with Ø = 12 mm and a bed height of 10 cm. Using a conventional flow rig, the dynamic adsorption capacities were determined in dry conditions using a concentration of approximately 100 ppm H_2S and a flow rate of 1000 mL min^{-1}. H_2S level in the outlet stream was continuously determined by a Varian CP4900 micro-GC.

3. Results and discussion

3.1. Photocatalytic degradation of H_2S: findings and challenges

The characterization of sol–gel TiO_2 films (TiO_2-A) on transparent substrates and their performance in the abatement of H_2S under different conditions have been deeply analysed by the authors [10,11,25]. TiO_2 xerogel obtained from the sol synthesised by route A and thermally treated at 350 °C consisted of TiO_2-anatase crystal phase with a minor TiO_2-brookite contribution. The main crystal size estimated by the Scherrer equation was 7.3 nm. The incorporation of TiO_2 to the support resulted in a decrease in the transmittance in the 300–500 nm wavelength range, associated with the semiconductor band-gap.

The evolution of H_2S conversion and selectivity to SO_2 obtained with a TiO_2-A coated plate at different water vapour contents is represented in Fig. 1. The concentration of H_2S was 15 ppm and the total gas flow rate was 75 mL min^{-1}. H_2S concentration was stabilized in the dark until the steady state condition was reached (not shown).

The initial activation period observed was a transient state consequence of surface transformations caused by the UV irradiation: photocatalytic oxidation of minor organic residues remaining from the synthesis process, but also photodesorption phenomena – for example of adsorbed water – [28,29] and sulphate accumulation on the surface may contribute to the initial modification observed [30]. The steady state was not reached during the photocatalytic degradation of H_2S. Instead, after a maximum, the photocatalytic activity decreased due to SO_4^{2-} accumulation on the catalytic surface [31,32]. SO_2 selectivity was related to the activity and the adsorption properties. There was a progressive and exponential increase of SO_2 release into the outlet stream up to stabilization (Fig. 1, right).

The results indicate the beneficial effect of the presence of hydroxyl groups in the photocatalytic performance. The addition of water vapour to the gas stream led to a significant reaction rate increase up to an optimum water vapour content of 1.3% (30% relative humidity at 30 °C), with H_2S conversion near 80%. As it was previously observed, water vapour content above this value was detrimental for hydrogen sulphide removal, due to competitive adsorption of H_2O and H_2S molecules for the same active sites [33].

Adsorption/desorption mechanisms of the species involved in the reaction such as H_2O, H_2S, SO_2 and SO_4^{2-} should be known in order to rationalize the obtained results, but not much information can be found in the literature concerning this topic for TiO_2 substrates. It is usually accepted that molecular water adsorption takes place on acid Lewis sites (Ti^{4+}), while dissociative adsorption, via hydrogen bond formation, implies basic Lewis sites with a proton abstraction [34]. H_2S molecule is similar to H_2O, but less likely to form hydrogen bonds and its protons are more acidic [35]. Therefore H_2S adsorption must be similar to that of H_2O and favoured in basic environments, according to H_2S adsorption studies on activated carbon [36]. SO_2 is adsorbed on acid and basic alumina adsorption sites [32] and a similar mechanism for titania may be expected. Sulphate is strongly adsorbed [37] and is considered a non-volatile compound.

The mechanism for photocatalytic H_2S oxidation could begin with its molecular adsorption and HS radical formation. The generation of these radicals in photosensitised sulphides oxidation is generally accepted. Sulphide redox potentials are +1.8 V versus the normal hydrogen electrode, lower than those of photogenerated electron holes from TiO_2, which have +3 V [38]. Nevertheless in presence of humidity electron holes react preferentially with water. It would not be expected that H_2S reacts directly with the electron holes (Eq. (9)) but with hydroxyl radicals (Eq. (10)), in a surface reaction equivalent to the atmospheric one [39,40].

$$h^+ + H_2S_{ads} \rightarrow H_2S^{+\bullet}_{ads} \leftrightarrow HS^{\bullet}_{ads} + H^+ \quad (9)$$

$$OH^{\bullet}_{ads} + H_2S_{ads} \rightarrow HS^{\bullet}_{ads} + H_2O_{ads} \quad (10)$$

It can be proposed that HS radicals react with oxygen to form SO_2 (Eqs. (11) and (12)), that can desorb or react with O_2 to form SO_3 (Eq. (13)). The fast SO_3 hydration reaction to form sulphuric acid prevents any escape of gaseous SO_3.

$$HS^{\bullet}_{ads} + O_{2\,ads} \rightarrow HSOO^{\bullet}_{ads} \quad (11)$$

$$HSOO^{\bullet}_{ads} + O_{2\,ads} \rightarrow SO_{2\,ads} \quad (12)$$

$$2SO_{2\,ads} + O_{2\,ads} \rightarrow 2SO_{3\,ads} \quad (13)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (14)$$

Since the process takes place in gas phase, the ${SO_4}^{2-}$ formed remains adsorbed on the active sites, leading to the deactivation of the photocatalyst. Moreover, the deactivation is fast because of the low photocatalyst amount and the low available surface per gram of photocatalyst, lower than for suspended photocatalysts.

As conclusion, the main drawback of these TiO_2 thin films for H_2S elimination is the formation of SO_2 and the deactivation by H_2SO_4 accumulation. Sulphur dioxide is toxic, corrosive and malodorous and the accumulation of ${SO_4}^{2-}$ on the photocatalyst surface leads to deactivation of the semiconductor.

3.2. *First strategy: photoactivity regeneration*

In general there are two main types of deactivation phenomena. One, reversible, is due to weakly adsorbed compounds or partially oxidized products. These species can be easily eliminated by a current of air, a moderate temperature increase or UV irradiation. The other, irreversible, is due to the deposition of non-volatile compounds, such as sulphates in the case of reactions involving H_2S. Thus, the regeneration of the photocatalysts was attempted by two different approaches. First, UV irradiation and an air flow containing 1.3% water vapour were applied; however, as expected, this approach was unsuccessful. The latter approach consisted of cleaning the surface with water, which is an easy and cheap alternative to conventional thermal treatments. In Fig. 2 the regeneration cycles of 112 glass rings coated with TiO_2-A are represented. A total gas flow of 600 mL min^{-1} with 35 ppm H_2S and 1.3% H_2O was treated during 5 cycles. After each use, the catalyst was rinsed three times with 100 mL distilled water.

The pH of the water recovered after the rinsing process decreased and the ionic chromatography analysis confirmed the presence of dissolved sulphate species from the surface of the catalysts. As it can be observed in Fig. 2, this simple regeneration process led to the recovery of the activity of the photocatalysts.

In order to optimize the rinsing procedure, equal amounts of used rings were treated in distilled water under agitation varying the following parameters: time (from 0 to 8 min), agitation rate (between 0 and 150 rpm), water volume (from 10 to 50 mL) and pH (neutral, basic or acid), as reported elsewhere [10]. The method was tested at two different temperatures, 25 and 50 °C. The efficiency of the process was evaluated by determination of the sulphate concentration in the water. The amount of water, agitation time and agitation rate were found not to be determinant factors in the process (data not shown). This is so because most of the sulphate was recovered in the water from the first rinsing step (see Fig. 3). On the other hand, sulphate removal rate was accelerated and the total amount of sulphate increased, when the wash proceeded at high temperature and pH, because under these conditions TiO_2 affinity for ${SO_4}^{2-}$ is diminished.

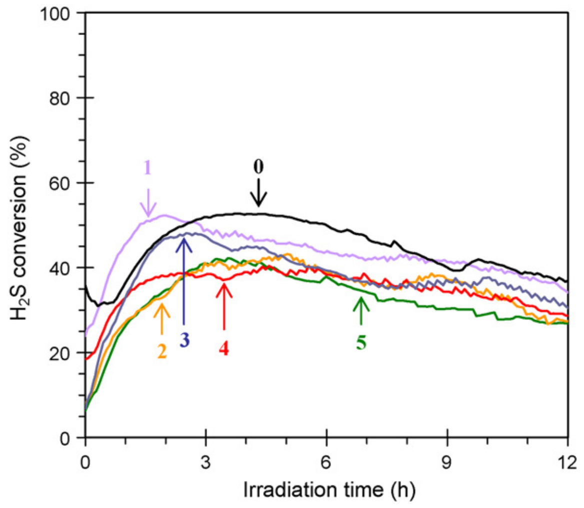

Fig. 2. Regeneration of TiO_2-A photocatalytic rings with distilled water during 5 consecutive deactivation and regeneration cycles.

The results obtained demonstrate that treating the photocatalyst with water reduced the surface acidity and removed the sulphur compounds accumulated on the catalyst surface. Thus, this method seems to be a good alternative for catalysts regeneration, ensuring the catalyst activity at least during five cycles.

3.3. *Second strategy: selective photocatalysts*

The properties of the photocatalyst were tailored using sol–gel route B in order to investigate the effect of porosity and doping on the selectivity and deactivation of the samples. TiO_2 porous samples were prepared using two different surfactants, Brij58 and F127, and compared with a reference dense sample. The incorporation of the surfactant led to thicker layers (~250 nm) than those obtained in the reference material (200 nm). Mesopores between 15 and 30 nm and pore volumes of 20–25% (v/v) were obtained in TiO_2-Brij58 and TiO_2-F127 coatings, respectively. XPS analysis showed bands at 284.6 eV, characteristic of C(sp^3), and 288.0 eV characteristic of C=O. The sample prepared with F-127 showed the highest amount of C=O, indicating that the surfactant was only partially

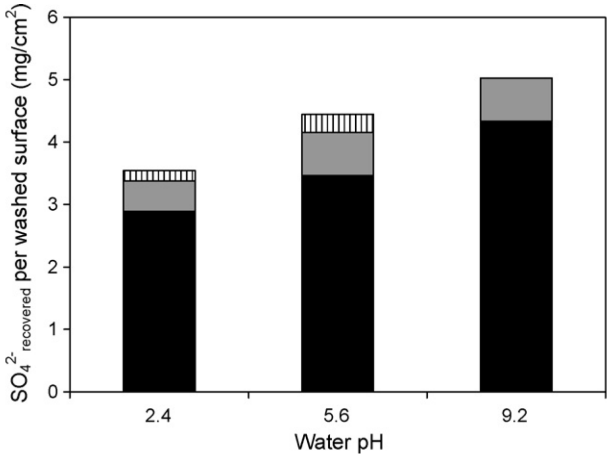

Fig. 3. Sulphate amount contained in the water of the photocatalyst rinsing process at different pH. First (black) second (grey) and third (dashed) rinses.

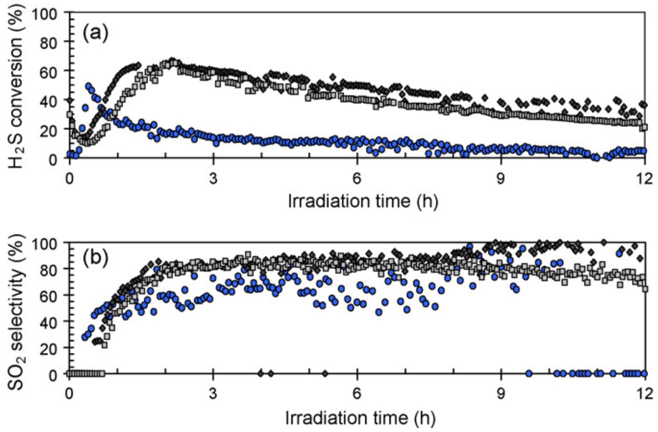

Fig. 4. (a) H_2S removal and (b) SO_2 formation for dense and porous samples synthesized by route B: TiO_2-Brij58 (♦), TiO_2-F127 (■), and TiO_2-dense (●).

removed during the calcination process. Both samples presented TiO_2-anatase.

Photocatalytic degradation of H_2S together with SO_2 formation is shown in Fig. 4a and b, respectively.

From the results depicted in Fig. 4, the beneficial effect of porosity in the photocatalytic activity of TiO_2-B is clear. H_2S conversion for samples prepared either with Brij58 or F127 showed a remarkable increase with respect to the dense sample and was close to that of TiO_2-A samples, but with only 2/3 of exposed coated surface (18 cm^2 instead of 27 cm^2). Photocatalytic activity reached a maximum value of around 67% for both porous samples, followed by the previously observed deactivation period. Almost all H_2S eliminated was oxidised to SO_2, resulting in a slower deactivation than for TiO_2-A samples. After 12 h irradiation, the conversion was around 30–40%, the half of the maximum value obtained, while TiO_2-A samples, that presented lower selectivity to SO_2, and thus enhanced sulphate formation, reduced their activity to ca. 20%, a quarter of the value obtained at the maximum. Therefore, materials with high SO_2 selectivity could be a good alternative to inhibit photocatalyst deactivation. In this case, the use of an adsorbent could avoid the release of SO_2 into the atmosphere.

Samples prepared with Brij58 were also synthesised using W and Ca as dopants in order to enhance the photocatalyst performance. Specifically, the former was used to activate the photocatalyst in the visible region and the latter to increase the surface basicity and therefore the adsorption of H_2S. The photocatalytic activity was not improved. In fact, the incorporation of these dopants to the TiO_2 coating was detrimental for the H_2S removal (data not shown). Other dopants or doping method should be investigated in order to improve these results. In a similar approach, other materials have been tested in the degradation of H_2S. Portela et al. reported the performance of powdered TiO_2/M-MCM-41 molecular sieves with M = Ce and Cr [12]. Ceria incorporation did not improve the photocatalytic activity, but chromium containing samples presented high initial photoactivity and were able to photooxidize H_2S without formation of SO_2 as by-product. Furthermore, the photocatalytic performance of these materials was even better under visible radiation. Nevertheless, fast deactivation occurred as a consequence of product accumulation on the photocatalytic surface. According to an XPS analysis, the reduction of Cr^{6+} to Cr^{3+} contributes to the progressive decrease in H_2S conversion with time. These materials, highly selective to sulphate, are very attractive since they could work without complementary adsorption units. Nevertheless further research is needed, since powdered chromium containing samples may pose a problem during the rinse with water in the regeneration step.

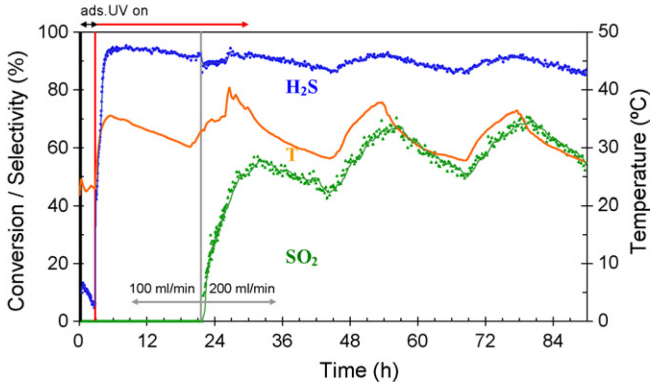

Fig. 5. Evolution of H_2S conversion (blue), SO_2 selectivity (green) and temperature (orange) for the TiO_2-SiMgOx coated material. Operating conditions: $H_2S = 15$ ppm, $H_2O = 1.3\%$, $t_r = 3.6$ and 1.8 s (100, 200 mL min^{-1}, respectively). (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)

3.4. *Third strategy: hybrid composites with enhanced adsorption capacity*

Materials combining adsorptive and photocatalytic properties are interesting alternatives to retain any undesired by-product in order to avoid external adsorption units [19,20]. The first hybrid materials studied consisted in a double layer composed by TiO_2 P25 deposited onto an adsorbent, SiMgOx. The results obtained with this composite are shown in Fig. 5, where the evolution of H_2S conversion, SO_2 selectivity and temperature were followed during more than three days. The same test was performed for the SiMgOx sample without the TiO_2 layer. The initial adsorption period was similar, but the activity under irradiation was negligible in the absence of the semiconductor.

An initial adsorption period of three hours was required to reach adsorption values below 5%. Then UV lamps were turned on and H_2S conversion rapidly increased above 90% without release of SO_2. Total conversion was not reached, probably due to mass transfer limitations. H_2S degradation values kept approximately constant during more than 18 h with no detection of any sulphur compound during this period. Since the activation of the H_2S oxidation reaction is not thermal but photonic, the significant effect of slight temperature variations should be mainly related to changes in the adsorption/desorption phenomena and not in the intrinsic reaction kinetics. At higher temperature, the increase in SO_2 selectivity could be related to its easier desorption. On the contrary, H_2S adsorption, limited by the competition of water vapor and H_2S for the active sites, might be favoured because of the decreased water vapor adsorption [10].

In order to know the photocatalytic behaviour in more severe conditions, thereafter the residence time was reduced to 1.8 s and the experiment was followed during near three days. In spite of the high and constant H_2S conversion values, the low residence time promoted the release of SO_2. This seems to indicate that only TiO_2 was acting and that the migration of SO_2 from TiO_2 to the adsorbent was limited by the low residence time. In order to promote the synergetic effect between adsorption and photocatalysis and to take advantage of the coated hybrid materials properties, adequate residence times are required to guarantee no diffusional problems.

Alternative hybrid materials are incorporated composites, where both components are mixed before the extrusion process [19]. Incorporated TiO_2–SiMgOx samples with ratio 1:1 were synthesised and tested for its conventional adsorption capacity. The dynamic adsorption capacity test can be seen in Fig. 6. Pure TiO_2–SiMgOx adsorbed H_2S for 187 min before emitting more than 5 ppm H_2S. This corresponds to a dynamic adsorption capacity

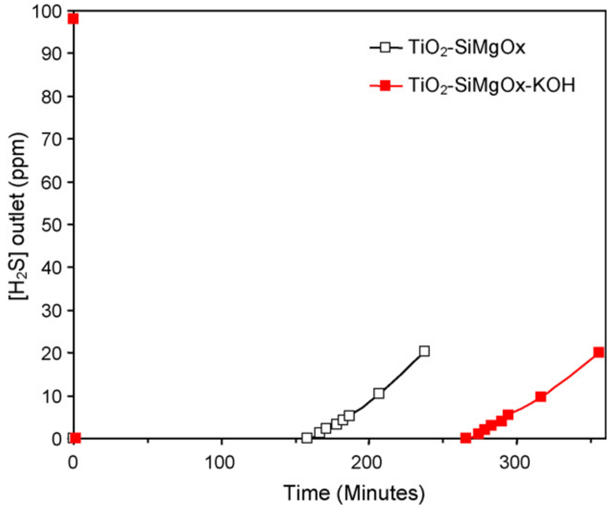

Fig. 6. Conventional adsorption capacity of TiO_2–SiMgOx hybrid material before and after washing with KOH.

of 4.8 mg H_2S per gram adsorbent. Then the used TiO_2–SiMgOx sample was washed in a 1 M KOH solution, whereby the sulphur compounds were extracted and new basic sites introduced. Thereafter, the dynamic adsorption capacity increased to 8.2 mg H_2S per gram adsorbent (295 min), almost the double of the original capacity.

The SiMgOx part of the composite works as a clay adsorbent. This facilitates the removal of surface H_2S from TiO_2, leaving the adsorption sites available for new H_2S molecules. Therefore, TiO_2–SiMgOx hybrid composite materials exhibit interesting adsorption capacities. It is clear that they are able to capture H_2S in an efficient manner, and thus play an important role in a hybrid adsorption/photocatalytic H_2S cleaning system [41]. Furthermore the regeneration procedure of washing with the alkaline KOH solution, not only restores the original activity but in fact enhances the capacity of the adsorptive material, introducing basic sites capable of attracting the acidic H_2S in greater amounts.

These TiO_2–SiMgOx incorporated samples were tested for photocatalysis. The results are shown in Fig. 7, where H_2S conversion values obtained during 24, 48 and 72 h are represented for three use/regeneration cycles. With the fresh composite, H_2S conversion of 40% was attained without SO_2 formation. This time a progressive decrease of the H_2S conversion with reaction time was observed but without any formation of SO_2. The intimate contact between the adsorbent and the photocatalyst may favour SO_2 retention. The homogeneous distribution of the photocatalyst in the whole material instead of the surface may explain the lower conversion and faster deactivation compared to what was observed in the coated hybrid material, where deactivation did not occur for a long time, even when SO_2 appeared.

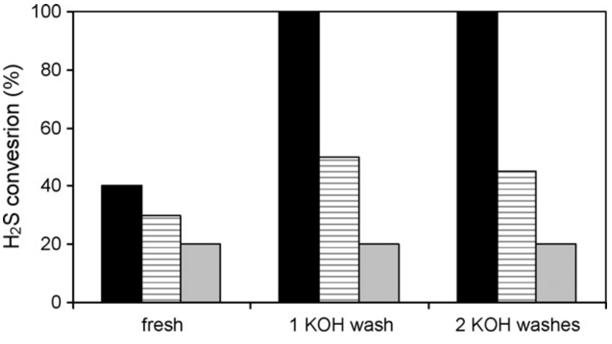

Fig. 7. H_2S conversion (mean values) for 24 h (black), 48 h (dashed) and 72 h (grey) on stream for TiO_2–SiMgOx incorporated composites. Activities measured for the sample fresh, after the first wash with KOH solution and after the second wash. Operating conditions: H_2S = 15 ppm, H_2O = 1.3%, t_r = 3.6 s.

In order to recover the photoactivity, the regeneration of the material was attempted by using a 1 M KOH basic solution. The wash process not only recovered but also promoted the photocatalytic activity, in a similar manner as observed above for conventional adsorption. H_2S conversion reached values near 100% due to the incorporation of basic sites that favoured H_2S adsorption. After three days of reaction, conversion values were similar to those obtained for fresh samples. The results seem to indicate that the basic centres were poisoned, probably by the formation of potassium sulphate. Nevertheless these centres can be easily regenerated or induced again with a subsequent KOH wash.

4. Conclusions

The chemical nature of the pollutant determines the strategy to be used in order not only to improve the efficiency and durability of the photocatalyst but also to obtain the desired selectivity. Several alternatives may be of interest. During photocatalytic H_2S oxidation, TiO_2-based supported photocatalysts deactivate over time due to sulphate accumulation and SO_2 is generated as an undesired by-product. Activity regeneration by washing with water has been proven to be effective and can even be enhanced by the use of basic solutions. Increased adsorption capability may solve the problem of SO_2 release and prolong the catalyst lifetime. The combination of an efficient photocatalyst, like P-25 TiO_2, and an adsorbent that may act as support, like SiMgOx, improves the photocatalytic efficiency with no SO_2 formation over extended periods of time. Therefore, hybrid materials constitute a promising alternative for H_2S elimination, due to the coupling of photocatalytic and adsorptive properties.

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