Photocatalytic-based strategies for H$_2$S elimination

R. Portela$^a$,*, S. Suárez$^a$, S.B. Rasmussen$^b$, N. Arconada$^c$, Y. Castro$^c$, A. Durán$^c$, P. Ávila$^b$, J.M. Coronado$^{a,1}$, B. Sánchez$^a$

$^a$ CIEMAT-PSA, Environmental Applications of Solar Energy, Avda Complutense, 22 Building 42, 28040 Madrid, Spain
$^b$ Instituto de Catálisis y Petroquímica-CSIC, C/Marie Curie 2, 28040 Madrid, Spain
$^c$ Instituto de Cerámica y Vidrio-CSIC, C/Kelsen 5, 28049 Madrid, Spain

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ABSTRACT

The mechanism of H$_2$S 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$_2$–SiMgO$_x$ 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$_2$S 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.

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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 case of wastewater treatment facilities, where fatal episodes can occur during maintenance routines [2].

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$_2$S, 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$_2$S to sulphate through the following mechanism, where electrons and holes are trapped by adsorbed water, superficial OH$^-$ and O$_2$ [8,9]:

\[
\text{TiO}_2 + h\nu \rightarrow h^+ + e^- \quad (1)
\]

\[
h^+ + H_2O_{ads} \rightarrow OH^+ + H^+ \quad (2)
\]

\[
h^+ + OH_{superf} \rightarrow OH^+ \quad (3)
\]

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

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

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

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...
deactivation. Moreover, in previous works the formation of $\text{SO}_2$ as gaseous reaction product has been reported [10–12]. As in the case of $\text{H}_2\text{S}$, 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.

$\text{TiO}_2$ 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 $\text{TiO}_2$ 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 $\text{TiO}_2$ 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 $\text{SiMgO}_x$. 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 $\text{H}_2\text{S}$ 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 $\text{SO}_2$-selective photocatalysts with slow deactivation; finally, the improvement of the adsorption capability of the photocatalyst through hybrid composites, which might avoid $\text{SO}_2$ release into the environment and/or prolong the life of the photocatalyst.

2. Materials and methods

Different commercial and synthesized $\text{TiO}_2$, alone or as part of $\text{TiO}_2–\text{SiMgO}_x$ 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 $\text{TiO}_2$ 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 ($\text{H}_2\text{O}:\text{HNO}_3$-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 $\text{TiO}_2$ was 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 $\text{SiO}_2$ [26,27] (200 nm) to avoid the diffusion of $\text{Na}^+$ cations from the glass substrate to the $\text{TiO}_2$ coating during the firing. These samples are named $\text{TiO}_2–\text{F}127$, $\text{TiO}_2–\text{Brij}58$ and $\text{TiO}_2–\text{dense}$.

Additionally, $\text{W}$ and $\text{Ca}$ doped samples were prepared incorporating 0.5% molar of tungsten (II) dichloride (WC1$_2$) and 3% molar of calcium nitrate (Ca(NO$_3$)$_2$) to sols B prepared with Brij58.

2.2. Preparation of $\text{TiO}_2$ 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.

$\text{TiO}_2$ 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 $\text{SiO}_2$ [26,27] (200 nm) to avoid the diffusion of $\text{Na}^+$ cations from the glass substrate to the $\text{TiO}_2$ coating during the firing. These samples are named $\text{TiO}_2–\text{F}127$, $\text{TiO}_2–\text{Brij}58$ and $\text{TiO}_2–\text{dense}$.

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 $\text{TiO}_2$-anatase (G–5, Millenium) and $\text{SiMgO}_x$ (sepiolite, Tolsa S.A.) or pure $\text{SiMgO}_x$ with water [19,20]. The optimum $\text{TiO}_2$ to $\text{SiMgO}_x$ 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 $\text{TiO}_2$ 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 $\text{TiO}_2–\text{SiMgO}_x$, containing 20 mg of $\text{TiO}_2$ ($\text{TiO}_2–\text{SiMgO}_x$ incorporated sample) and two of $\text{SiMgO}_x$. A suspension of P25 $\text{TiO}_2$ from Degussa in 2-propanol was prepared to coat one of the $\text{SiMgO}_x$ samples with 20 mg of $\text{TiO}_2$ to obtain the $\text{TiO}_2–\text{SiMgO}_x$ coated sample.

For the adsorption study similar $\text{TiO}_2–\text{SiMgO}_x$ 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 $\text{H}_2\text{S}$ 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
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. H₂S in N₂ 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 H₂S, 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. H₂S conversion and selectivity to SO₂ were calculated according to Eqs. (7) and (8):

\[ X_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}}} \times 100 \]  
\[ S_{\text{SO}_2} = \frac{[\text{SO}_2]_{\text{outlet}} - [\text{H}_2\text{S}]_{\text{inlet}}}{[\text{H}_2\text{S}]_{\text{outlet}}} \times 100 \]  

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

### 2.5. Conventional H₂S adsorption measurements

For evaluation of the adsorption capacity of the hybrid TiO₂–SiMgOₓ composite the fraction of material with sizes 4.4 mW cm⁻² was determined 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. H₂S conversion and selectivity to SO₂ were calculated according to Eqs. (7) and (8):

\[ X_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}]_{\text{inlet}} - [\text{H}_2\text{S}]_{\text{outlet}}}{[\text{H}_2\text{S}]_{\text{inlet}}} \times 100 \]  
\[ S_{\text{SO}_2} = \frac{[\text{SO}_2]_{\text{outlet}} - [\text{H}_2\text{S}]_{\text{inlet}}}{[\text{H}_2\text{S}]_{\text{inlet}}} \times 100 \]  

### 3. Results and discussion

#### 3.1. Photocatalytic degradation of H₂S: findings and challenges

The characterization of sol–gel TiO₂ films (TiO₂–A) on transparent substrates and their performance in the abatement of H₂S under different conditions have been deeply analysed by the authors [10,11,25]. TiO₂ xerogel obtained from the sol synthesised by route A and thermally treated at 350 °C consisted of TiO₂-anatase crystal phase with a minor TiO₂-brookite contribution. The main crystal size estimated by the Scherrer equation was 7.3 nm. The incorporation of TiO₂ 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 H₂S conversion and selectivity to SO₂ obtained with a TiO₂-A coated plate at different water vapour contents is represented in Fig. 1. The concentration of H₂S was 15 ppm and the total gas flow rate was 75 mL min⁻¹. H₂S 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 H₂S. Instead, after a maximum, the photocatalytic activity decreased due to SO₄²⁻ accumulation on the catalytic surface [31,32]. SO₂ selectivity was related to the activity and the adsorption properties. There was a progressive and exponential increase of SO₂ 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 H₂S 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 H₂O and H₂S molecules for the same active sites [33].

Adsorption/desorption mechanisms of the species involved in the reaction such as H₂O, H₂S, SO₂, and SO₄²⁻ should be known in order to rationalize the obtained results, but not much information can be found in the literature concerning this topic for TiO₂ substrates. It is usually accepted that molecular water adsorption takes place on acid Lewis sites (Ti⁴⁺), while dissociative adsorption, via hydrogen bond formation, implies basic Lewis sites with a proton abstraction [34]. H₂S molecule is similar to H₂O, but less likely to form hydrogen bonds and its protons are more acidic [35]. Therefore, H₂S adsorption must be similar to that of H₂O and favoured in basic environments, according to H₂S adsorption studies on activated carbon [36]. SO₂ 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 H₂S 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 TiO₂, which have +3 V [38]. Nevertheless in presence of humidity electron holes react preferentially with water. It would not be expected that H₂S 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].

\[
\begin{align*}
\text{h}^+ + \text{H}_2\text{S}_{\text{ads}} & \rightarrow \text{H}_2\text{S}^*_{\text{ads}} \leftrightarrow \text{HS}^-_{\text{ads}} + \text{H}^+ \quad (9) \\
\text{OH}^*_{\text{ads}} + \text{H}_2\text{S}_{\text{ads}} & \rightarrow \text{HS}^-_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \quad (10)
\end{align*}
\]

It can be proposed that HS radicals react with oxygen to form SO₂ (Eqs. (11) and (12)), that can desorb or react with O₂ to form SO₃ (Eq. (13)).

\[
\begin{align*}
\text{HS}^-_{\text{ads}} + \text{O}_2 & \rightarrow \text{HSO}_2^-_{\text{ads}} \quad (11) \\
\text{HSO}_2^-_{\text{ads}} & + \text{O}_2 \rightarrow \text{SO}_2_{\text{ads}} \quad (12) \\
2\text{SO}_2_{\text{ads}} + \text{O}_2 & \rightarrow 2\text{SO}_3^-_{\text{ads}} \quad (13) \\
\text{SO}_3^- + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 \quad (14)
\end{align*}
\]

Since the process takes place in gas phase, the SO₄²⁻ 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 TiO₂ thin films for H₂S elimination is the formation of SO₂ and the deactivation by H₂SO₄ accumulation. Sulphur dioxide is toxic, corrosive and malodorous and the accumulation of SO₄²⁻ 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 H₂S. 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 TiO₂-A are represented. A total gas flow of 600 mL min⁻¹ with 35 ppm H₂S and 1.3% H₂O 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).

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. TiO₂ porous samples were prepared using two different surfactants, Brij58 and TiO₂-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 TiO₂–Brij58 and TiO₂-F127 coatings, respectively. XPS analysis showed bands at 284.6 eV, characteristic of C(sp³), 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. 2. Regeneration of TiO₂-A photocatalytic rings with distilled water during 5 consecutive deactivation and regeneration cycles.](Image)

![Fig. 3. Sulphate amount contained in the water of the photocatalyst rinsing process at different pH. First (black) second (grey) and third (dashed) rinses.](Image)
Photocatalytic degradation of H₂S together with SO₂ 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 TiO₂-B is clear. H₂S 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 TiO₂-A samples, but with only 2/3 of exposed coated surface (18 cm² instead of 27 cm²). Photocatalytic activity reached a maximum value of around 67% for both porous samples, followed by the previously observed deactivation period. Almost all H₂S eliminated was oxidised to SO₂, resulting in a slower deactivation than for TiO₂-A samples. After 12h irradiation, the conversion was around 30–40%, the half of the maximum value obtained, while TiO₂-A samples, that presented lower selectivity to SO₂, and thus enhanced sulphate formation, reduced their activity to ca. 20%, a quarter of the value obtained at the maximum. Therefore, materials with high SO₂ selectivity could be a good alternative to inhibit photocatalyst deactivation. In this case, the use of an adsorbent could avoid the release of SO₂ 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 H₂S. The photocatalytic activity was not improved. In fact, the incorporation of these dopants to the TiO₂ coating was detrimental for the H₂S 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 H₂S. Portela et al. reported the performance of powdered TiO₂/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 photocactivity and were able to photooxidize H₂S without formation of SO₂ 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 Cr⁶⁺ to Cr⁴⁺ contributes to the progressive decrease in H₂S 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.

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 TiO₂-P25 deposited onto an adsorbent, SiMgOₓ. The results obtained with this composite are shown in Fig. 5, where the evolution of H₂S conversion, SO₂ selectivity and temperature were followed during more than three days. The same test was performed for the SiMgOₓ sample without the TiO₂ 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 H₂S conversion rapidly increased above 90% without release of SO₂. Total conversion was not reached, probably due to mass transfer limitations. H₂S degradation values kept approximately constant during more than 18h with no detection of any sulphur compound during this period. Since the activation of the H₂S 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 SO₂ selectivity could be related to its easier desorption. On the contrary, H₂S adsorption, limited by the competition of water vapor and H₂S 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 H₂S conversion values, the low residence time promoted the release of SO₂. This seems to indicate that only TiO₂ was acting and that the migration of SO₂ from TiO₂ 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 TiO₂–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 TiO₂–SiMgOₓ adsorbed H₂S for 187 min before emitting more than 5 ppm H₂S. This corresponds to a dynamic adsorption capacity
of 4.8 mg H₂S per gram adsorbent. Then the used TiO₂–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 H₂S 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 H₂S from TiO₂, leaving the adsorption sites available for new H₂S molecules. Therefore, TiO₂–SiMgOₓ hybrid composite materials exhibit interesting adsorption capacities. It is clear that they are able to capture H₂S in an efficient manner, and thus play an important role in a hybrid adsorption/photocatalytic H₂S 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 H₂S in greater amounts.

These TiO₂–SiMgOₓ incorporated samples were tested for photocatalysis. The results are shown in Fig. 7, where H₂S conversion values obtained during 24, 48 and 72 h are represented for three use/regeneration cycles. With the fresh composite, the H₂S conversion of 40% was attained without SO₂ formation. This time a progressive decrease of the H₂S conversion with reaction time was observed but without any formation of SO₂. The intimate contact between the adsorbent and the photocatalyst may favour SO₂ 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 SO₂ appeared.

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. H₂S conversion reached values near 100% due to the incorporation of basic sites that favoured H₂S 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 H₂S oxidation, TiO₂-based supported photocatalysts deactivate over time due to sulphate accumulation and SO₂ 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 SO₂ release and prolong the catalyst lifetime. The combination of an efficient photocatalyst, like P-25 TiO₂, and an adsorbent that may act as support, like SiMgOₓ, improves the photocatalytic efficiency with no SO₂ formation over extended periods of time. Therefore, hybrid materials constitute a promising alternative for H₂S elimination, due to the coupling of photocatalytic and adsorptive properties.

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