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Madrid, Spain, March 28th, 2011

Dear Editor:

I am writing to submit the manuscript entitled “Photocatalytic oxidation of methyl ethyl ketones over sol-gel mesoporous and meso-structured TiO$_2$ films obtained by EISA method” by N. Arconada, Y. Castro, A. Durán and V. Héquet.

Looking forward to hearing from you soon.

Sincerely yours,

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Photocatalytic oxidation of methyl ethyl ketones over sol-gel mesoporous and meso-structured TiO$_2$ films obtained by EISA method

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Abstract

This work reports the influence of the meso-structure of TiO$_2$ films in the photocatalytic oxidation of methyl ethyl ketone. Five types of TiO$_2$ films were prepared combining the sol-gel route with the EISA method. Sols were prepared from titanium tetrachloride (TiCl$_4$) using different types of pore generating agents. The characterisation was performed by Fourier Transform Infrared Spectroscopy (FTIR), Grazing X-Ray diffraction (GXRD), X-ray diffraction of small angle and Transmission Electron Microscopy (FE-SEM). Spectral Ellipsometry studies were performed to obtain the adsorption/ desorption isotherms and calculate porous size distribution, pore volume and specific surface area ($S_s$) of the films. Kinetic of MEK photocatalytic oxidation data were modelled by Langmuir–Hinshelwood equation and the adsorption and kinetic constants (k and K) were calculated. Better results of MEK degradation were obtained for the Brij58 films deposited at RH of 20% and 50% films. The results obtained were correlated with the porosity properties of the films.

**Keywords:** TiO$_2$ anatase films, sol-gel, evaporation induced self assembly method (EISA), mesoporous order of the films, MEK degradation
1. INTRODUCTION
Indoor pollution is of increasing concern in urban societies since much people spend most of their time (between 70 – 90 %) into closed areas (building and transports) [1-6]. Indoor air quality (IAQ) is affected by many factors among which the presence of volatile organic compounds (VOCs) well known for their toxic effects on human health [7-9]. Currently, a great interest is focused in developing processes that can reduce or eliminate VOCs, purifying indoor environments. Photocatalytic oxidation is a promising method to destroy these compounds [10-12].

Among the semiconductors, TiO$_2$ is one of the best candidates. Its band gap energy is around 3.2 eV, thus it can be photo-activated in the near UV region also it is a cheap, nontoxic and highly stable semiconductor [13,14], permitting the formation of highly reactive species that can oxidize VOCs adsorbed on the catalyst surface [10,15,16].

Numerous studies deal with TiO$_2$-based photocatalysts in the form of powder or pellets [17,18], this involving several technical problems like that they can not be used in continuous engineering processes, because a step of filtration after the reaction is necessary. For this reason, TiO$_2$ films have been proposed. Sol-gel process is considered as an efficient method to prepare homogeneous films [19]. This technique presents some advantages compared to other methods such as homogeneity at molecular level, easy control of the composition, low temperature of sintering, good adherence, priority crystallization of anatase and good optical properties. Nevertheless, the reported results show that the photocatalytic efficiency of thin TiO$_2$ sol-gel catalysts has to be improved. One way is to produce porous and meso-structure TiO$_2$ films by adding pore generating agents able to create porous structures with high specific surface area which will increase the active area, and the contact between pollutants and catalyst, this improving the degradation of VOCs [20-28]. “Evaporation Induced Self Assembly” (EISA) method is reported as a suitable method to obtain meso-porous ordered films by sol-gel
This method involves the preparation of a sol containing the inorganic precursor in acidic medium and in presence of ethanol, water and a suitable surfactant. During the deposition of the sol, the controlled evaporation of volatile solvent allows the sol to gel transition and the self-assembly of surfactant micelles, leading to a three-dimensional network deposited as a thin film with ordered mesoporous structure. The elimination of the surfactant by calcination, washing or other techniques, creates stable and ordered mesoporous films with high specify surface area [30-32].

There is some literature dealing with the photocatalytic oxidation of ketones (acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) or methyl isopropyl ketone (MIPK)) using supported-TiO$_2$ catalysts, and most of these papers focuses on the influence of water vapour on the degradation of these compounds [3,33]. However, the effect of the structure and characteristic of the TiO$_2$ catalyst has been rarely reported [34,35]. Raillard et al. has studied the influence of different types of TiO$_2$-based catalysts (Degussa P25 TiO$_2$ films on glass support, TiO$_2$-anatase on fibrous support, mixed of SiO$_2$/TiO$_2$ deposited onto cellulose supports, or dense TiO$_2$ sol-gel films) in the degradation of ketones in the photocatalytic oxidation of MEK [24,36] and toluene [37] showing that the stabilising agent, the type of glass plates, the number of coatings and the temperature of sintering are important aspects affecting the efficiency of the catalyst oxidation. Coronado et al. [38] study the photocatalytic behaviour in gas phase for TiO$_2$ sol-gel thin films supported on glass rings using acetone and MIBK as model molecule. Finally, Vicent et al. [39] developed a special photocatalytic reactor to reduce VOCs emissions into indoor air where the catalyst consisted in TiO$_2$ Degussa P25 deposited on fibre-glass substrates. The lack of information in literature related to the study of photocatalytic properties of TiO$_2$ porous thin films increases the importance of the work here reported about these catalysts.
Thus, the aim of this work is to study the degradation of methyl ethyl ketone in gas phase using mesoporous and meso-structured TiO\textsubscript{2} films obtained by sol-gel method combined with the evaporation induced self-assembly method (EISA). Three types of no-ionic pore generating agents were incorporated to sols: Pluronic (F127), polyethylene glycol hexadecyl ether P5884 (Brij58) and Triton X100 (Triton). The films were deposited by dip-coating controlling the relative humidity and the withdrawal rates. Different techniques were used to perform the structural characterisation by: Environmental Ellipsometric Porosity (EEP) measurements from which it is possible to obtain the adsorption and desorption isotherms, to calculate porous size distribution, pore volume, specific surface area ($S_s$) and exposed surface area ($S_{exp}$), and study the ordered of the mesoporosity by TEM and Low-X-ray diffraction. A batch photocatalytic reactor was used to evaluate the photocatalytic activity of TiO\textsubscript{2} coatings at dry air and a fixed temperature and varying the pollutant concentrations. The structure of the films (porosity properties and meso-porous order) and photocatalytic parameters (adsorption and kinetic constants) have been considered to correlate the film structure with the efficiency as photocatalytic materials.

2. EXPERIMENTAL

2.1. Preparation of the TiO\textsubscript{2} sols and coatings

Titania sols were prepared using titanium tetrachloride (TiCl\textsubscript{4}) as precursor, previously mixed with absolute ethanol in a molar relation TiCl\textsubscript{4}/EtOH = 1/5. Different types of surfactants Pluronic F-127 (F127), polyethylene glycol hexadecyl ether P5884 (Brij58) and Triton X100 (Triton) dissolved in absolute ethanol were incorporated to the sol in a molar ratio F127/TiCl\textsubscript{4} = 0.005, Brij58/TiCl\textsubscript{4} = 0.1 and Triton/TiCl\textsubscript{4} = 0.3. Finally, de-ionised water was added drop by drop onto the sols, up to a final oxide
concentration of 27 g/L. The final molar ratios were: 1TiCl₄: 62.5EtOH: (0.005, 0.1 and 0.3) Surfactant: 10H₂O.

A reference sol was also prepared following a similar process but adding only a minimum amount of surfactant to obtain a good wettability between the sol and substrate, with a final oxide concentration of 27 g/L.

TiO₂ films were deposited onto glass-slides by dip-coating combined with the EISA method. Table 1 summarizes the relative humidity and the withdrawal rate of deposition for all the compositions. In the case of F127 sols, where the relative humidity of 20-70% is indicated, the films were obtained by dipping at 20% RH, and after a first drying the RH was increased up to 70%, and maintained during 24 hours.

The glass-slides were coated with a first layer of quasi-dense SiO₂ [40,41] (thickness of ~218 nm, and refractive index of ~1.44) to inhibit the diffusion of Na⁺ cations from the substrate to TiO₂ coating during heat treatment [42-44].

The films were sintered following a cycle of 130°C/1day and 350°C/90min to consolidate the structure. The dip-coating procedure was repeated and a second layer was deposited in the same conditions with a final heat treatment of 130°C/1day, 350°C/3h and 500°C/10 min to eliminate the surfactants and to crystallise TiO₂ in anatase form.

### 2.2. Structural characterization of TiO₂ coatings

The coatings were characterised by Optical Microscopy (Zeiss, HP1), Grazing incident X-Ray Diffraction (range of 2θ = 20-70°, fixed time of 20 s/step and increment of 0.05°, Panalytical X’Pert PRO theta/theta equipment) and Fourier Transform Infrared Spectroscopy (transmission mode in frequency range of 4000-400 cm⁻¹, resolution of 2 cm⁻¹, Perkin Elmer FTIR Spectrum 100 equipment) to confirm the homogeneity, the elimination of surfactants, the crystallisation of the inorganic network as TiO₂-anatase,
and to determine the crystal size of using the Scherrer’s equation. Finally, Transmission Electronic Microscopy (Hitachi H-7100) and Low-X-Ray Diffraction (range of 2θ = 0.5-5°, fixed time of 1.5 s/step and increment of 0.01°, Bruker D8 Advance equipment) were used to study the meso-structuration of TiO₂ films.

2.3. Textural characterisation of TiO₂ coatings

Thickness (e) and refraction index (n) were measured using a Spectroscopic Ellipsometer (WVASE32, (“Variable Angle Spectroscopic Ellipsometer”) J.A. Co., Woollam M-2000UTM). A humidity controlled chamber was used to evaluate the variation of e and n as a function of relative humidity (RH) (from 0 to 100%). The absorption-desorption isotherms were obtained, and pore size distribution and pore volume of the films were determined, using the Bruggeman Effective Medium Approximation (BEMA) model and the modified Kelvin’s equation. Specific surface area (Sₘ) and exposed surface (Sₑₓᵖ) of the films were calculated from this date as well [45].

2.4. Photocatalytic activity of TiO₂ films

The photocatalytic activity of TiO₂ films was evaluated through the degradation of methyl ethyl ketone (MEK, Aldrich 99.5% purity) in gas phase at a fixed temperature of 30 (± 1) °C. Figure 1 shows the 12-L bath reactor used for the photocatalytic measurements. In all the experiments, four samples with a total area of 40 cm² were introduced into the reactor.

UV irradiation was provided by a medium pressure mercury lamp (Heraeus TQ 718 Z4, 700 W, 𝜆ₘₐₓ = 365 nm) refrigerated by a water cooling tube. The temperature was maintained constant using a water circulation on the outer side of the reactor. Different thermocouples were used to control the temperature at different points in the
reactor. Relative humidity was fixed at 0-3%, using a dry air flow, being measured with a thermohygroimeter at the beginning of each experiment. The gas was mixed in the reactor with a circulating loop fed with an all-Teflon pump (flow of 10 L.min$^{-1}$). The pollutants were introduced in the system as liquids through a septum on the top of the reactor and were immediately volatilized. Five MEK initial concentrations between 0.06 and 1.34 g/m$^3$ were introduced into the reactor for each set of experiments. A gas chromatograph associated with a flame ionization detector (GC-FID) was used to follow MEK concentrations during the experiments. Gas samples were withdrawn with airtight syringes. Reference runs were conducted with samples and no light activation (adsorption) and with light in absence of TiO$_2$ film semiconductor (photolysis).

3. RESULTS AND DISCUSSION
3.1. TiO$_2$ sols and catalyst characterization

Homogeneous, transparent and stable TiO$_2$ sols were obtained following the process previously described [46]. TiO$_2$ thin films with high optical quality, transparency and without precipitates were deposited by dip-coating combined with the EISA method at different relative humidity and withdrawal rates.

The crystallisation of the inorganic network as TiO$_2$-anatase was confirmed by GXRD and FTIR studies. For all the coatings the absence of TiO$_2$-rutile phase and the complete removal of surfactant were verified after the heat treatment. The crystallite size (D) of the coatings was estimated using the Scherrer’s equation and the peak at $2\theta$ = 25.2, selected as the main peak for determining anatase phase. Table 1 summarises the crystallite size obtained for all the films. Crystal size of 30 nm was obtained for dense reference film and between 16 to 19 nm for the porous films, indicating that the presence of surfactant inhibits the growth of crystallites as well as the aggregation of adjacent particles, thus resulting highly porous [47].
Transmission Electronic Microscopy (TEM) and Low angle X-Ray Diffraction (XRD) were used to confirm the porous structure of the films and verify the order of the meso-porous.

*Figure 2* shows the micrographs of the films obtained with sol a) F127 at RH 20-70%, b) Brij58 at RH 50% and c) Triton at RH 50%, after the heat treatment. The films obtained with F127 sol at RH 20-70% and Brij58 sol at RH 50% show a perfect meso-structured porosity. However, the film obtained with Triton RH 50% shows a high porosity with homogeneous porous size, but without any order. Finally, the film obtained with the reference sol (not shown) is not porous being so considered like a reference dense film.

Low angle X-Ray Diffraction patterns confirm the results obtained by TEM analysis. *Figure 3* shows the diffractograms of films obtained with Brij58 sol at RH 50% and F127 sol at RH 20-70%, showing two peaks, around $2\theta = 0.8^\circ$ for Brij58 and around $2\theta = 1.8^\circ$ for F127, both associated with the ordered porosity. The presence of peaks in this range indicates the ordered mesoporosity of the films.

*Table 1* summarises the structural data obtained by TEM and Low- X-ray Diffraction for all the coatings indicating like dense, meso-porous or meso-structured coatings.

### 3.2. Textural properties of TiO₂ coatings

Spectral ellipsometry and Environmental ellipsometric porosimetry (EEP) measurements were used to determine thickness, refraction index and porosity properties of the films. This is a non destructive method based on the adsorption-desorption isotherms obtained from the variation of thickness and refractive index induced by the change of water partial pressure above a film [45].

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Figure 4 shows the adsorption/desorption isotherms obtained by EEP and using the Bruggeman Effective Medium Approximation model (BEMA) along with PSD for the films obtained with the TiO\textsubscript{2} sols a) Brij58 at RH 20%, b) Brij58 at RH 50%, c) F127 at RH 20-70% and d) Triton at RH 50%. A typical behaviour of mesoporous materials (pore diameter range between 2-50 nm), associated with isotherms of type IV, is observed for all the coatings. For Figures 4a-d the isotherms present hysteresis loops related with the capillary condensation of water that occurs in the meso-pores. According to IUPAC, hysteresis loops are classified into four types (H1-H4). Type H1 loop exhibits parallel and nearly vertical branches, characteristic of materials with cylindrical pore geometry and/or a highly uniform pore size. Hysteresis loops of type H2 present triangular shape and a steep desorption branch attributed to pore connectivity effects [48] which are often considered a result of the presence of pores with narrow mouths (bottle-neck pores) [49]. Coming back to Figure 4, hysteresis loops H1 are identified in Figure 4a, 4c and 4d and H2 in Figure 4b [49,50].

Figure 4 also includes the corresponding PSD, determined using the Kelvin’s equation [45]. Total volume of pores between 30-45 % vol. and pores sizes distributions in the range 2.4-6.4 nm were obtained for all the films. Triton at RH 50% films show a broad pore size distribution and the lower hysteresis loop in the isotherms indicates smaller pore medium pore size (2.4 nm). On the other side, F127 at RH 20-70% coatings present narrower pore size distribution corresponding to the meso-structuration of porosity. Finally, meso-structured films prepared with Brij58 at RH 50% show a bimodal pore size distribution, with pores around 1 nm and 2.6 nm, the former indicating the presence of bottle-neck pores.

Specific surface area ($S_a$) was calculated considering an ellipsoidal-sphere geometry pore and using the slopes $\beta$ ($\beta_{\text{microporous}}$ and $\beta_{\text{mesoporous}}$) of the t-plot curve, as well as the
pore size ($\phi$) and pore volume ($V_{pore}$) [45]. Finally, the exposed area ($S_{exp}$) has been estimated taking into account $S_s$, thickness and size of the coatings. This last parameter represents the total area exposed to irradiation, thus being relevant to photocatalytic behaviour.

Table 1 summarises the values of pore size, pore volume and specific and exposed surface areas ($S_s$, $S_{exp}$) for all the films.

3.3. MEK photocatalysis oxidation
The kinetic study was performed on the five photocatalysts. The photocatalytic experiments were carried out with five different MEK concentrations, at fixed temperature (30º C), under fixed dry atmospheric conditions (RH $\leq$ 3%) and UV lamps irradiation. Methyl ethyl ketone (MEK) initial concentrations were in a range of 0.06 to 1.34 g/m$^3$. Figure 5 shows the decrease of MEK concentration (C (g/m$^3$)) with the irradiation time with the films Brij58 at RH 50%.

No adsorptions (around 0%) were obtained for the Brij58 at RH 50% and Triton at RH 50% photocatalysts. Adsorptions around 10% were obtained for Brij58 at RH 20% and Reference photocatalyst. At last, F127 at RH 20-70% shows high adsorption values around 30% after 150 minutes.

In photocatalytic studies, kinetic of degradation is generally represented by the Langmuir-Hinshelwood (L-H) model, defined by the following (Equation 1):

$$r_0 = \frac{kKC_0}{1+KC_0}$$

Equation 1

where $r_0$ is the initial reaction rate (g m$^{-3}$ min$^{-1}$), $k$ the reaction kinetic constant (g m$^{-3}$ min$^{-1}$), and $K$ is the Langmuir adsorption constant (m$^3$ g$^{-1}$).
The degradation of MEK ($C_0 = 0.34 \text{ g/m}^3$) were performed under dry air and ambient temperature, without UV irradiation (adsorption in dark conditions) and without TiO$_2$ films under irradiation (photolysis) for all the photocatalysts. Fast photocatalytic degradation rates of MEK were obtained for all the photocatalysts after periods of measurement of 150 minutes with few photolysis around 5%.

The initial reaction rates ($r_0$) were calculated for each experiment by modelling the kinetics of degradation by a third-order polynomial and its derivative form at initial time $r_0 = (dC/dt)_{t=0}$. The Langmuir-Hinshelwood constant are determined by least square analysis. Figure 6 shows the experimental points modelled by the Langmuir-Hinshelwood equation for the whole photocatalysts.

Table 2 summarises the percentage of adsorption, L-H model adsorption, kinetic constants and kinetic constant normalized per cm$^2$ of film, obtained for all the photocatalysts.

The results of the different tested materials can be explained from the kinetic and also from the absorption values. Concerning the kinetic constant ($k$), Brij58 at RH 20% films presents the best capacity of degradation, followed by Brij58 at RH 50%. On the other side, the adsorption constant ($K$) is the higher for Brij58 at 50% films followed by Reference > Triton at RH 50% > Brij58 at RH 20% > F127 at RH 20-70% films.

Initial reaction rate ($r_0$) of the kinetic of degradation is closely related and changes a lot with the concentration of MEK contaminant. At low concentration, the kinetic is controlled by the mass transfer (adsorption) of the molecule and the materials with higher adsorption constant $K$ will be the most efficient. However, at high contaminant concentrations the kinetic constant $k$ controls the reaction rate since the surface is often near saturation; thus, materials with higher $k$ will show the highest photocatalytic capacity.
In our samples, Brij58 at RH 20% films induce the highest degradation at high initial concentration while Brij58 at RH 50% samples present the most efficient behavior at lower initial MEK contents. The other tested compositions show the same order at low and high MEK concentrations. The efficiency of the photocatalysis follows the order Reference > Triton RH 50% > F127 RH 20-70%.

The different photocatalytic behaviour observed between Brij58 at RH 20% and RH 50% could be explained considering the adsorption-desorption isotherms and PSD. In the case of meso-structured Brij58 at RH 50% films, the presence of a pore size distribution of 2.6 nm pores along with bottle necks 1 nm in size may justify the high efficiency at low MEK concentrations; for increasing pollutant contents, the narrow bottle-necks will rapidly arrive to saturation by molecules adsorption thus implicating the fall of the photocatalytic activity. On the other hand, Brij58 at RH 20% films present a similar pore size distribution without pore narrowing. Thus, the efficiency will increase at higher MEK concentrations obtaining faster photocatalytic degradation.

Finally, films of Triton at RH 50% and F127 at RH 20-70% present a similar behaviour, related to the dense TiO$_2$-anatase material. Triton films show a similar PSD and wide pore range although the lower hysteresis indicates smaller pore size. On the other side, Triton films have only 216 nm, the thinnest among all the studied coatings. This means that the exposed area, close related to thickness, is smaller, likely explaining the rapid saturation through adsorption. In the case of F127 samples, their poor photocatalytic behaviour could be related to the lower specific and exposed surface areas, resulting from the higher pore size. Besides this textural reasons, the orientation of porous channels is often referred as parallel to the substrate [51,52], this possibly hindering the access of the pollutant to the porous structure. The control of the porosity orientation is
thus a key feature to solve, in order to improve the photocatalytic behaviour of these materials.

4. Conclusions

- Mesoporous TiO$_2$-anatase films were prepared combining the sol-gel route with the EISA method using F127, Brij58 and Triton as surfactants.
- FTIR and GXRD confirmed the tetragonal TiO$_2$-anatase phase as only crystalline phase in all the films. F127 at RH 20-70% and Brij58 at RH 50% films present a perfect meso-structuration confirmed by low angle XRD and TEM.
- Spectral ellipsometry and Environmental ellipsometric porosimetry (EEP) were used to calculate the adsorption/desorption isotherms and to estimate total pore volumes between 30 to 45 %, PSD around 2.4 – 6.4 nm, and exposed surface areas of 90-120 m$^2$.
- The photocatalytic behaviour of MEK degradation depends on the initial concentration of contaminant and the textural properties of the films such as pore volume, specific and exposed surface areas.
- Brij58 at RH 50% films present the most efficient behavior at lower initial MEK contents while Brij58 at RH 20% coatings induce the highest degradation at high initial concentration. The meso-structured films Brij58 at RH 50% show narrow bottle-necks which arrive to saturation for increasing pollutant contents; this justifying the high efficiency at low MEK concentrations.
- Fast MEK degradation was obtained for all the catalyst with a few contribution of photolysis (around 5%), although the highest photocatalytic activity was attained for films Brij58 at RH 20% and RH 50%.
- Present and previous results on other gas pollutants confirm this type of coatings as promising systems to indoor air quality (IAQ) applications.
References


Table 1. Composition, withdrawal & RH of deposition, thickness (e), refraction index (n), density, structure porosity, crystal size (D), pore volume ($V_{\text{pore}}$), medium pore size ($\Phi$) and specific ($S_s$) and exposed ($S_{\text{exp}}$) surface area after the heat treatment.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>RH (%)</th>
<th>Extraction rate (cm.min$^{-1}$)</th>
<th>e (nm) ± 0.02</th>
<th>n (at $\lambda = 700$nm) ± 0.05</th>
<th>Structure</th>
<th>D (nm) ± 10%</th>
<th>$V_{\text{pore}}$ (%) ± 5%</th>
<th>$\Phi_{\text{medium}}$ (nm) ± 10%</th>
<th>$S_s$ (m$^2$/cm$^3$) ± 10%</th>
<th>$S_{\text{exp}}$ (m$^2$) ± 10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>20</td>
<td>25</td>
<td>150</td>
<td>2.06</td>
<td>Dense</td>
<td>30</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Brij58</td>
<td>20</td>
<td>35</td>
<td>302</td>
<td>1.67</td>
<td>Meso-porous</td>
<td>16</td>
<td>40</td>
<td>2.8</td>
<td>320</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td>270</td>
<td>1.68</td>
<td>Meso-structured</td>
<td>19</td>
<td>34</td>
<td>1 and 2.6</td>
<td>315</td>
<td>122</td>
</tr>
<tr>
<td>F127</td>
<td>20-70</td>
<td></td>
<td>400</td>
<td>1.59</td>
<td>Meso-structured</td>
<td>19</td>
<td>45</td>
<td>6.4</td>
<td>202</td>
<td>87</td>
</tr>
<tr>
<td>Triton</td>
<td>50</td>
<td>11</td>
<td>216</td>
<td>1.65</td>
<td>Meso-porous</td>
<td>19</td>
<td>38</td>
<td>2.4</td>
<td>340</td>
<td>136</td>
</tr>
</tbody>
</table>
Table 2. Composition, % adsorption, Langmuir-Hinshelwood kinetic (k) and adsorption (K) constants, for all the photocatalysts

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>RH deposition (%)</th>
<th>Adsorption (%) at 150min.</th>
<th>k (g m(^{-3}) min(^{-1}))</th>
<th>k (x10(^{-4})) (g m(^{-3}) min(^{-1})/cm(^2) films)</th>
<th>K (m(^{-3}) g(^{-1}))</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>20</td>
<td>11</td>
<td>0.0027 (±0.0003)</td>
<td>2.2 (± 0.2)</td>
<td>10.0 (±2.85)</td>
<td>0.975</td>
</tr>
<tr>
<td>Brij58</td>
<td>20</td>
<td>14</td>
<td>0.0044 (±0.0003)</td>
<td>3.5 (± 0.2)</td>
<td>4.3 (±0.83)</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0</td>
<td>0.0028 (±0.0001)</td>
<td>2.2 (± 0.8)</td>
<td>16.6 (±3.48)</td>
<td>0.983</td>
</tr>
<tr>
<td>F127</td>
<td>20-70</td>
<td>27</td>
<td>0.0024 (±0.003)</td>
<td>1.9 (± 0.2)</td>
<td>3.6 (±1.55)</td>
<td>0.977</td>
</tr>
<tr>
<td>Triton</td>
<td>50</td>
<td>0</td>
<td>0.0026 (±0.0003)</td>
<td>2.4 (± 0.2)</td>
<td>7.8 (±3.05)</td>
<td>0.978</td>
</tr>
</tbody>
</table>
Figure 1. Photocatalytic batch reactor
Figure 2. TEM micrographs for the films obtained with the TiO$_2$ sols: a) F127 at RH 20-70%, b) Brij58 at RH 50% and c) Triton at RH 50%
Figure 3. XRD small angle spectra for the films obtained with Brij58 sols at RH 50% and F127 sols at RH 20-70%
Figure 4. Adsorption/desorption isotherms (● □ axes: $V_{\text{ads}}/V_{\text{film}}$ vs $P/P_o$) and pore size distribution (■ axes: Dv/Dr vs pore diameter) for the films obtained with TiO$_2$ sols; a) Brij58 at RH 20%, b) Brij58 at RH 50%, c) F127 at RH 20-70% and d) Triton at RH 50%.
Figure 5. MEK concentration (C (g/m$^3$)) versus the irradiation time (minutes) for the films of Brij58 at RH 50%.
Figure 6. $r_0$ vs $C_0$ for the photocatalysts and the reference modelled by Langmuir-Hinshelwood equation.
The photocatalytic behaviour of mesoporous and meso-structured TiO$_2$ films was studied by heterogeneous oxidation of MEK. Textural properties of the catalysts (pore volume, pore size distribution and specific and exposed surface areas) are key features to explain the photocatalytic efficiency.
**Research Highlights**

1. Mesoporous and meso-structured TiO$_2$ films were obtained by sol-gel/EISA method.

2. F127/RH 20-70 and Brij58/RH 50 were the only meso-structured resulting coatings.

3. MEK degradation depends on C$_o$ concentration and textural properties of the films.

4. The highest photocatalytic activities were obtained for films Brij58 at RH 20/50.