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On the comparison of photocatalysts activity: A novel procedure for the measurement of titania surface in TiO_2/SiO_2 materials

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Abstract

The distribution of two different phases in a mixed oxide material could be investigated through several physicochemical characterization techniques. However, the estimation of the fraction of the total surface area corresponding to each oxide is a very difficult task. In this work, we present a novel procedure for the determination of the titanium dioxide surface in titania–silica materials. This new method is based on the measurement of the phosphorus content of the mixed oxide after reaction with phenylphosphonic acid. The quantification of the TiO_2 surface has permitted the comparison of the catalytic activity of different materials in processes in which titanium dioxide is the only catalytically active phase and silica behaves as an inert support, as, for instance, in photocatalytic reactions. The activity of several TiO_2/SiO_2 photocatalysts for cyanide and methanol photooxidation have been analysed and compared with pure TiO_2 materials in terms of equal mass of semiconductor, photonic efficiency and active surface area. The results suggest the possibility of achieving surface activity rates even higher than the material Degussa P25 when using nanocrystalline titania supported on silica.

Keywords: Catalyst activity; Photocatalysis; Titania–silica; Titania surface

1. Introduction

The assessment of titania catalysts activity is a subject not standardized in the literature. Several ways have been usually applied for the comparison of the photocatalytic degradation rates of a test pollutant with different catalytic materials. It is widely accepted that the correct scientific procedure to achieve this goal is the evaluation of the true quantum yield, that is the ratio between the observed reaction rate and the volumetric rate of absorption of photons by the material [1]. The experimental difficulties that arise in the determination of the absorbed photon flux usually require of the adoption of radiation absorption models for the tested catalysts [2,3].

Due to the technical hitches previously mentioned, the use of equal mass catalyst concentrations in the suspension is the most common procedure to compare the activity of different semiconductor materials [4,5], or to test the influence of the synthesis route on the activity of titania catalysts [6]. A similar practice is based on the specific activity referred to the mass of the catalyst [7].

It is well-known that the specific surface area of the semiconductor is one of the most important factors in the photocatalytic activity [8], especially in liquid phase systems [9]. For that reason, the intrinsic activity referred to the BET surface area (S_{BET}) of the material has been also proposed for comparative studies [10]. But in photocatalytic processes, titania also needs high degree of crystallinity, which usually leads to a compromise between both factors [11,12]. This could be the reason to explain the absence of a direct correlation between the photoactivity and the BET surface area for different TiO_2 samples found by several research groups [13–15].

It is also recognized that a suitable way of increasing the effective TiO_2 surface area is through a homogeneous dispersion on a silica support [16,17]. In these cases, the simple question of how to compare the activity of supported and unsupported materials or among different supported systems is even more difficult to answer than for the comparison of powder titania. A similar approach to the procedure commonly used with pure titania samples is the use of a constant mass of

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semiconductor material [18,19]. However, to the best of our knowledge, the comparison of the activity of supported photocatalysts in terms of the effective titania surface has never been used, what is probably related to the difficulty of its determination.

The characterization of metal oxides catalysts is usually crucial because of the strong dependence of the synthesis procedure on the properties of the prepared materials. The distribution of two different phases in mixed oxide materials such TiO_2/SiO_2 catalysts can be investigated through powder X-ray diffraction, transmission electron microscopy, Raman spectroscopy, UV–vis diffuse reflectance spectroscopy, etc. However, the only approach reported in the literature to establish the fraction of the total surface area corresponding to each oxide is based on the temperature-programmed desorption (TPD) of 2-propanol coupled with thermogravimetric and mass spectrometry detection (TGA-MS) [20]. According to this procedure, the amount of 2-propanol adsorbed and decomposed to propene and water is considered to be proportional to the surface area of titania as the interaction with silica is very weak.

In this work, we present a novel procedure for the determination of the titanium dioxide surface area in titania–silica mixed oxides, based on the reaction of phosphonic acids with titania reported by Mutin et al. [21] for the selective functionalization of TiO_2/SiO_2 materials. Assuming that the amount of phosphorus atoms incorporated to the material is proportional to the accessible titania surface area, we propose the estimation of the TiO_2 surface of titania–silica mixed oxides through the measurement of the phosphorus content of the catalyst after reaction with phenylphosphonic acid.

2. Methods

2.1. Catalysts synthesis and characterization

The silica-supported TiO_2 catalysts have been prepared employing a previously reported method [18]. The incorporation of TiO_2 clusters into the SiO_2 support was accomplished via a sol–gel route, starting with the required amount of titanium tetraisopropoxide, which is transformed to TiO_2 inside the porous structure of the support. The solids, recovered by centrifugation, were hydrothermally treated at 110 °C and further calcined at 550 °C.

Two different silica materials were used as supports: a commercially available non-structured silica (Grace Sylopol 2104, $GrSiO_2$, S_{BET} = 317 $m^2\ g^{-1}$) which presents a wide pore size distribution and the so-called SBA-15 silica (S_{BET} = 640 $m^2\ g^{-1}$), a mesostructured material with a very well defined pore size in the range of the mesopores (D_P = 6.0 nm). The latter was prepared in our laboratory according to the original method of Zhao et al. [22]. The catalysts will be named as $x\%TiO_2/GrSiO_2$ or $x\%TiO_2$/SBA-15, where x represents the nominal wt.% of titania loading.

The characterization of the samples by powder X-ray diffraction in a Philips X'PERT MPD diffractometer using Cu Kα radiation shows the presence of nanocrystalline clusters of anatase. The average crystal sizes estimated by applying the Scherrer equation to the (1 0 1) anatase peak at 25.3°, using calcite (1 0 4) signal at 29.4° as internal standard to calculate the instrumental width, were in the range of 6–12 nm depending on both the type of support and the titania loading. The BET specific surface areas of the materials obtained upon supporting TiO_2, estimated from the nitrogen adsorption–desorption isotherms at 77 K recorded in a Micromeritics Tristar 3000 equipment, were 299 $m^2\ g^{-1}$ for $20\%TiO_2/GrSiO_2$; 246 $m^2\ g^{-1}$ for $40\%TiO_2/GrSiO_2$; 179 $m^2\ g^{-1}$ for $60\%TiO_2/GrSiO_2$; 532 $m^2\ g^{-1}$ for $20\%TiO_2$/SBA-15; 442 $m^2\ g^{-1}$ for $40\%TiO_2$/SBA-15; 349 $m^2\ g^{-1}$ for $60\%TiO_2$/SBA-15. More details about the synthesis, characterization and activity of these materials are given elsewhere [18,23].

Finally, a material 100% titania was prepared following the same synthesis procedure in the absence of the silica support. This material will be referred as $100\%TiO_2$ and showed a specific surface area of 17.2 $m^2\ g^{-1}$ and anatase crystals with an average size of 46 nm.

2.2. Modification of the catalysts with phenylphosphonic acid

Modification of the surface of the synthesized TiO_2/SiO_2 materials with phenylphosphonic acid was carried out according to the procedure reported by Mutin et al. [21]. Five hundred milligrams of the mixed oxide powder were added to a flask containing 500 mL of a 4 mM solution of phenylphosphonic acid in a 4:1 CH_3OH:H_2O (v/v) mixture. After 24 h of vigorous stirring at room temperature, the solids were filtered and washed several times with methanol–water solutions and finally dried at 110 °C for 24 h.

Determination of the phosphorus content of the materials was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in a Varian Vista AX instrument. The catalysts were dissolved by attack with hydrofluoric acid and rinsed to a 50 mL volume with deionised water. The phosphorus concentration in the solution was quantified through its emission line at 213.618 nm after calibration with certified standards.

Solid-state ^{31}P MAS-NMR spectra were acquired on a VARIAN-Infinity 400 spectrometer operating at a frequency of 161.9 MHz with the following conditions: magic-angle spinning at 14 kHz; high-power proton decoupling; $\pi/2$ pulse, 1.7 μs; a repetition delay of 10 s; 2000 scans. Chemical shifts were referenced to 85% H_3PO_4 in water.

2.3. Photocatalytic experiments

The photocatalytic activity of these materials was evaluated using the photooxidation of methanol and potassium cyanide as test reactions. The experiments was carried out in a 1 L batch photoreactor irradiated by a 150 W medium pressure mercury lamp (Heraeus TQ-150) placed axially inside a quartz jacket externally cooled with a 0.01 M $CuSO_4$ aqueous solution to maintain the reaction media at 25 °C and cut-off the radiation below 325 nm. The catalyst was maintained in suspension by a magnetic stirrer placed at the bottom of the vessel. A gas

bubbling system provides the oxygen required for the oxidation reactions. For potassium cyanide photooxidation runs, air was continuously bubbled during the reaction. In contrast, for methanol photooxidation experiments, the suspensions were saturated with molecular oxygen prior to the addition of methanol and no gas bubbling was introduced during the reaction to avoid losses of the oxidation products by stripping from the liquid phase. At 25 °C, the theoretical concentration of oxygen in the saturated solution is 39.5 $mg_{O_2}\ L^{-1}$. In both test reactions, the oxidizable compound was added in the desired concentration and stirred in the dark for 30 min in order to reach the adsorption equilibrium prior to the irradiation. During this time, the lamp was switched on to stabilize the emission power and spectrum. The UV-A incident photon flow, determined by the ferrioxalate actinometry procedure, was 1.37×10^{-5} Einstein $L^{-1}\ s^{-1}$.

The initial conditions for the potassium cyanide photooxidation catalytic tests were a concentration of 3.85 mM KCN (Panreac, reagent grade) and pH value of 11.0, adjusted by addition of NaOH (Scharlab, reagent grade). The catalyst concentration was 0.5 $g_{TiO_2}\ L^{-1}$ for all the reaction tests, taking into account the different titania loading of the catalysts. This catalyst concentration has been previously selected from studies with Degussa P25 titania in order to reach a total absorption of photons. The decrease in free cyanide concentration along the reaction was followed by the pyridine-barbituric standard colorimetric method, based on the blue-red colour development (absorption maximum at 575 nm) upon addition of a pyridine-barbituric reagent [24]. For methanol photooxidation experiments, an initial concentration of 2 M was used, following the reaction by measuring the formaldehyde production employing the Nash method [25]. This method is based on the reaction of formaldehyde with acetylacetone and ammonia to form a coloured product with a maximum of absorbance at 412 nm, measured after an incubation time of 60 min. In both cases, prior to the analysis, the catalyst was removed from the sampled suspensions by using a 0.22 μm nylon syringe filter. A Merck Spectroquant VEGA 400 spectrophotometer was used for the absorption measurements.

3. Results and discussion

3.1. Determination of the titania surface area

Tables 1 and 2 summarize the main results obtained in the evaluation of the titania surface for the different studied materials. In addition to both silica supports, the 100%TiO_2 material and the six TiO_2/SiO_2 catalysts, two different commercial titania samples commonly used in photocatalytic studies have been employed: Degussa P25 TiO_2 (80% anatase, 20% rutile) and Aldrich TiO_2 (100% anatase). The ICP-AES measurements of the different digested samples allowed the determination of the phosphorus content of the material ($mg_P\ g^{-1}$) after reaction with phenylphosphonic acid following the procedure previously described in the experimental. From these values, the surface concentration in phosphorus atoms per square nanometer ($at_P\ nm^{-2}$) could be derived using the BET surface area of the materials. For every tested material, two replicates of the reactions with phenylphosphonic acid and ICP-AES measurements have been performed, in order to asses the reproducibility of the proposed procedure. As it can be seen, both values are very close for all the studied materials, leading in all cases to an error below 3 $m^2_{TiO_2}\ g^{-1}$ in the estimated TiO_2 surface.

Table 1
Phosphorus content of pure titania and silica materials after reaction with phenylphosphonic acid

Material	S_{BET}[a] ($m^2\ g^{-1}$)	Phosphorus content from ICP-AES		
		$mg_P\ g^{-1}$	$at_P\ nm^{-2}$	
Degussa P25 TiO_2	52	7.28	2.72	Average
		6.90	2.58	value 2.8 ± 0.2
Aldrich TiO_2	7.1	1.08	2.95	
		1.12	3.03	
100%TiO_2	17.2	2.54	2.87	
		2.26	2.55	
$GrSiO_2$	317	0.03	0.0019	Average value
		0.03	0.0021	0.002 ± 0.0002
SBA-15	640	0.07	0.0020	
		0.08	0.0023	

[a] Calculated from N_2 adsorption isotherm.

The estimation of the titania surface area of the TiO_2/SiO_2 materials is carried out following two assumptions:

(I) The number of phosphorus atoms determined by ICP-AES only depends on the titania surface area accessible to the reaction with phenylphosphonic acid. Therefore, small differences attributed to the specific titania crystalline phase or the surface properties, such as degree of hydroxylation, could be neglected for these measurements. This statement is supported by the results obtained for the phosphorus content of the three pure titania materials. As it can be observed, differences among them are similar to the experimental error of the measurement. Consequently, an average phosphorus surface density of 2.8 ± 0.2 atoms per square nanometer was obtained and adopted for any kind of titania surface (Table 1). This value is in agreement with the grafting density of 3 phenylphosphonic acid molecules nm^{-2} reported by Mutin et al. [21].

(II) The incorporation of phosphorus by reaction of phenylphosphonic acid with any kind of silica surface could be considered as negligible. This hypothesis is supported by the results reported in Table 1 for both pure silica materials, and it is the basis of the present procedure for the selective determination of the titania surface area of mixed TiO_2/SiO_2 materials.

According to these statements, the accessible TiO_2 surface areas of the six TiO_2/SiO_2 photocatalysts were calculated from the measured phosphorus content assuming a surface density of 2.8 $at_P\ nm^{-2}$. The results are reported in Table 2. The error associated to the estimated titania surface has been calculated by applying the conventional formulas for the uncertainty propagation from the experimental error of the phosphorus

Table 2
Titanium dioxide surface of TiO_2/SiO_2 materials determined by reaction with phenylphosphonic acid

Material	S_{BET}[a] ($m^2\ g^{-1}$)	D_{XRD}[b] (nm)	S_{XRD}[c] ($m^2\ g^{-1}$)	P content ($mg_P\ g^{-1}$)	TiO_2 surface ($m^2_{TiO_2}\ g^{-1}$)
20%TiO_2/$GrSiO_2$	299	6.8	41.9	2.12 2.07	14.6 ± 1.08
40%TiO_2/$GrSiO_2$	246	8.0	71.3	3.14 3.20	22.1 ± 1.61
60%TiO_2/$GrSiO_2$	179	12.2	70.1	4.99 5.03	35.0 ± 2.51
20%TiO_2/SBA-15	532	6.2	46.0	1.69 1.17	10.0 ± 2.69
40%TiO_2/SBA-15	442	6.7	85.1	2.54 2.11	16.2 ± 2.43
60%TiO_2/SBA-15	349	6.8	125.8	3.54 3.58	24.8 ± 1.79

[a] Calculated from N_2 adsorption isotherm.
[b] Average titanium dioxide crystal size determined by powder X-ray diffraction.
[c] Titania surface area estimated from the XRD average crystal size assuming spherical shape.

measurements and the error associated to the surface density calculated from the pure TiO_2 materials. It is important to notice, that these values correspond to the titania surface accessible to react with phenylphosphonic acid, which means that the actual titania surface could be higher in materials in which the diffusion of big molecules is restricted, such as the case of TiO_2/SBA-15 materials. A detailed explanation of the molecular sieve effect induced by the structure of these materials can be found in the literature [23].

From the results shown in Table 2, it is clearly observed that the surface area attributed to TiO_2 increases as the titanium dioxide loading does, as it was expected. The percentage of titania contribution to the total surface area of the material increases not only because of the higher TiO_2 surface area but also for the lower total surface area of the materials with higher titania loadings: 4.9% (20%TiO_2/$GrSiO_2$), 9.0% (40%TiO_2/$GrSiO_2$), 19.5% (60%TiO_2/$GrSiO_2$), 1.9% (20%TiO_2/SBA-15), 3.7% (40%TiO_2/SBA-15) and 7.1% (60%TiO_2/SBA-15). Comparing the results obtained with both silica supports, it can be observed that for equal titania loading the materials supported on SBA-15 show lower titania surface areas. A possible explanation of this fact is that not all the titanium dioxide surface of TiO_2/SBA-15 materials is accessible to phenylphosphonic acid due to the particular structure of these materials [23]. In contrast, the results obtained for the $GrSiO_2$-supported materials could be considered as more feasible, due to their non-structured porous networks.

Table 2 also shows the estimated surface area of the titania crystals assuming a non-porous spherical geometry with the average size determined from the X-ray diffraction. These values could be considered as the upper limit of the titania surface area. The actual values must be lower, as these crystals are supported on the silica, reducing their exposed surface. As it can be seen, the measured titania surface areas only account for a fraction of the S_{XRD} maximum value: 34.9% (20%TiO_2/$GrSiO_2$), 31.1% (40%TiO_2/$GrSiO_2$), 49.9% (60%TiO_2/$GrSiO_2$), 21.7% (20%TiO_2/SBA-15), 19.1% (40%TiO_2/SBA-15) and 19.8% (60%TiO_2/SBA-15). It is important to notice, that the materials supported on $GrSiO_2$ exhibit between a third and a half of this upper limit, whereas the materials supported on SBA-15 only reach a 20% of the maximum value, as a consequence of the diffusional restrictions to the access of phenylphosphonic acid molecules.

It has been proposed that the reaction of phenylphosphonic acid with titania takes place through the formation of bidentate and tridentate phosphonate species by condensation of the phosphonic group with the surface hydroxyls of titanium dioxide [21]. Fig. 1 shows the ^{31}P MAS-NMR spectra of Degussa P25 TiO_2, $GrSiO_2$ support and the three $TiO_2/GrSiO_2$ materials. In all cases, a resonance at 13.6 ppm is observed, ascribed to tridentate $PhP(OTi)_3$ species. The resonance at 19.4 ppm is attributed to phosphonate species with different bonding modes or in a distorted geometry [26]. The intensity of both signals is higher as the titania wt.% of the material

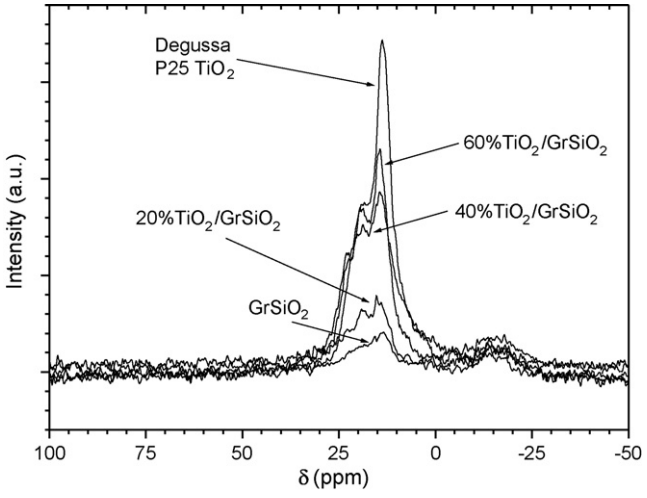

Fig. 1. ^{31}P MAS-NMR spectra of Degussa P25 TiO_2, the commercial $GrSiO_2$ silica support and three $TiO_2/GrSiO_2$ materials after reaction with phenylphosphonic acid.

increases, being for the silica support of the same low intensity than the signal at negative chemical shifts attributed to residual inorganic phosphorus species.

3.2. Comparison of the photocatalytic activity

The determination of the titania surface area of mixed TiO_2/SiO_2 oxides permits the comparison of activities among different photocatalysts on an active-semiconductor surface basis. The oxidation of diluted solutions of free cyanide ions has been used to test the activity of materials in which the access of big organic molecules could be restricted [23]. Concerning the oxidation of 2 M solutions of methanol, this reaction has been selected as it has shown a total scavenging of the photogenerated hydroxyl radicals [27]. As an example, Fig. 2 shows the concentration profiles determined for both reactions using Degussa P25 TiO_2. Methanol reactions have been followed through the formation of formaldehyde, as a total selectivity to this product has been reported until methanol is totally depleted [27]. In both cases, linear profiles have been obtained at the beginning of the reaction. Under these conditions, the reaction performance can be described by the initial reaction rate, r^0, calculated by fitting the experimental data to a zero order kinetics model. For methanol photooxidation reactions, that means that oxygen is not controlling the kinetics for irradiation times sufficiently low. After 15 min, the stoichiometric consumption of oxygen would be 12.5 mg_{O_2} L^{-1} (from the initial 39.5 mg L^{-1} of the saturated solution) and it must be taken into account that the experiments shown in Fig. 2 are the ones with higher conversions. At higher irradiation times, a decrease in the reaction rate attributed to the lower oxygen concentration in solution could be observed. For that reason, the analysis of the experimental data has been carried out under initial reaction conditions.

Table 3 summarizes the main results obtained in the photooxidation of cyanide and methanol with Degussa P25 TiO_2 and the six SiO_2-supported photocatalysts. The catalytic activity of the materials has been expressed in three different ways:

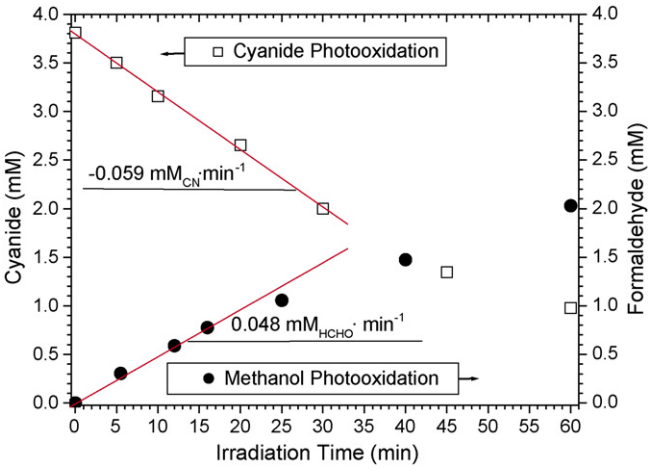

Fig. 2. Zero-order kinetics fit of cyanide and methanol photooxidation using Degussa P25 TiO_2.

(i) The initial reaction rate, r_1^0. This value has been calculated directly from the concentration profiles of CN^- and CH_3OH against time of irradiation. As equal TiO_2 mass concentration has been used in all the reactions, r_1^0 could be considered as the specific reaction rate (in fact, half of this value, as 0.5 g of TiO_2 have been used). The main problem of this parameter is that the values are very dependent on the specific photoreactor and radiation source.

(ii) The initial photonic efficiency, r_2^0. The ratio between the initial reaction rate and the volumetric incident photon flow allows the comparison of the results obtained by different research groups using similar catalysts and photoreactors, independently on the irradiation source. Both r_1^0 and r_2^0 must be considered to asses the efficiency of the process from an economical point of view, as they take into account the catalyst and electricity consumption.

(iii) The surface reaction rate, r_3^0. By referring the initial reaction rate to the active TiO_2 surface in the reactor, it is possible the comparison of the results obtained using very different catalysts configurations, such as TiO_2 powders, slurries of silica-supported photocatalysts, films, etc. The surface reaction rate is the parameter usually considered in

Table 3
Initial reaction rates for cyanide and methanol photooxidation using the different photocatalysts referenced to the same mass concentration of semiconductor (r_1^0), incident photon flux (r_2^0) and TiO_2 surface (r_3^0)

	Degussa P25 TiO_2	20%TiO_2/$GrSiO_2$	40%TiO_2/$GrSiO_2$	60%TiO_2/$GrSiO_2$	20%TiO_2/SBA-15	40%TiO_2/SBA-15	60%TiO_2/SBA-15	100%TiO_2
Catalyst concentration (g L^{-1})	0.50	2.50	1.25	0.87	2.50	1.25	0.87	0.50
TiO_2 surface (m^2 L^{-1})	26.0	36.4	27.5	30.2	24.8	20.2	21.5	8.6
3.85 mM CN^- photooxidation								
$r_1^0 \times 10^4$ (mol m^{-3} s^{-1})	9.87	4.82	5.47	6.31	6.60	7.14	8.37	4.57
$r_2^0 \times 10^2$ (mol Einstein^{-1})	7.22	3.52	4.00	4.61	4.83	5.23	6.12	3.35
$r_3^0 \times 10^8$ (mol $m_{TiO_2}^{-2}$ s^{-1})	3.80	1.32	1.99	2.09	2.66	3.54	3.89	5.31
2 M MeOH photooxidation								
$r_1^0 \times 10^4$ (mol m^{-3} s^{-1})	7.67	6.37	6.52	7.40	7.62	7.12	7.17	–
$r_2^0 \times 10^2$ (mol Einstein^{-1})	7.04	5.81	5.90	6.70	7.00	6.49	6.54	–
$r_3^0 \times 10^8$ (mol $m_{TiO_2}^{-2}$ s^{-1})	2.95	1.75	2.37	2.45	3.07	3.53	3.34	–

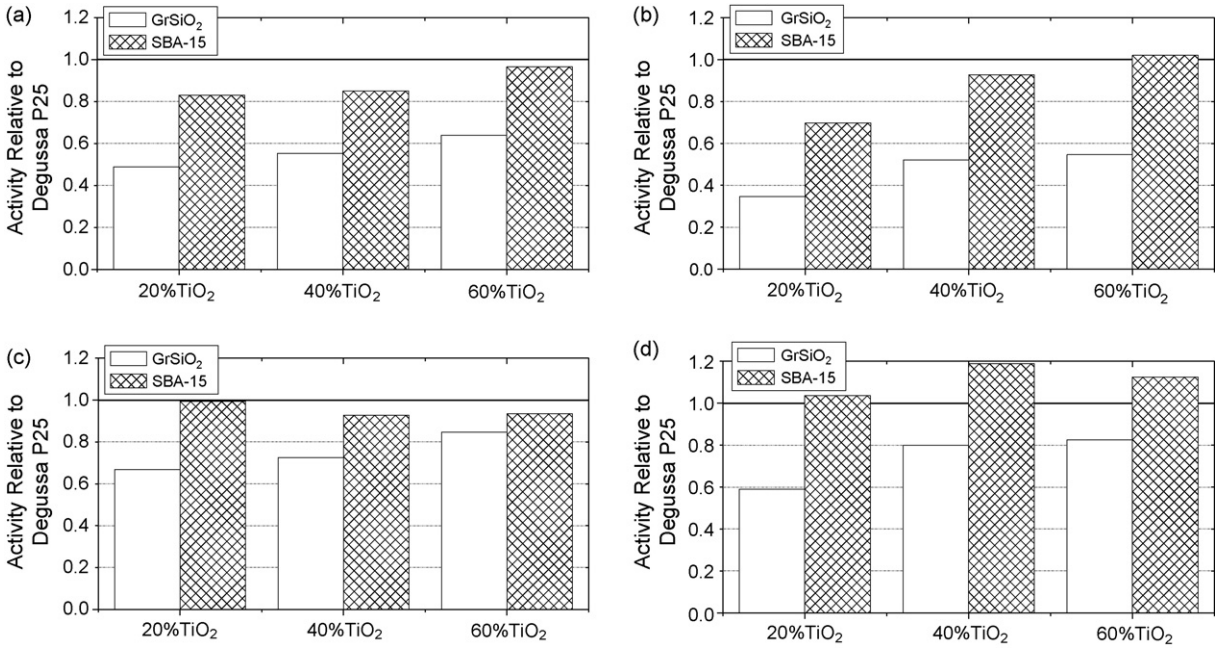

Fig. 3. Relative activity of TiO_2/SiO_2 photocatalysts as compared to Degussa P25: (a) 3.85 mM cyanide photooxidation rate; (b) surface-based 3.85 mM cyanide photooxidation rate; (c) 2 M methanol photooxidation rate; (d) surface-based 2 M methanol photooxidation rate.

the kinetic modelling of the heterogeneous catalytic reactions and chemical reactors engineering.

Fig. 3 depicts the relative activities of the supported photocatalysts in comparison with Degussa P25. All the synthesised materials are less active than Degussa P25 when they are compared in terms of initial reaction rates (same mass of semiconductor and incident photon flow), although TiO_2/SBA-15 materials reach relative activities close to 1. When compared in terms of the titania surface reaction rates, the materials supported on SBA-15 reach higher rates than Degussa P25, specially for high titania loadings. These activities could be suspicious of being overestimated because of the lower titania surface area values for TiO_2/SBA-15 materials derived from the diffusional restrictions to the access of phenylphosphonic acid above mentioned. However, as it can be observed, the material 100%TiO_2 shows a relative activity close to 50% in comparison with Degussa P25 in specific terms, whereas its surface reaction rate is 1.5 times higher. The reason of this high activity seems to be due to the properties of the titanium dioxide crystals achieved following the described hydrothermal synthesis procedure [28]. Consequently, the TiO_2/SiO_2 materials combine the high activity of the so-prepared titania crystals with the increase in active surface area derived from the homogeneous dispersion on the porous structure of the support.

The observed reaction rate has been reported to be very dependent on the test molecule, not only for the possible presence of diffusional restrictions [23] but also for the compromise between crystallinity and surface area affecting the adsorption and reaction stages [12]. From the results reported in Table 3, the molar reaction rate for cyanide photooxidation, either as r_1^0, r_2^0 or r_3^0, can reach values higher than the ones obtained for 2 M methanol solutions. This methanol concentration has been reported to produce the total scavenging of the photogenerated hydroxyl radicals [27], supporting the possibility of a direct hole transfer mechanism for cyanide photooxidation, in agreement with the proposal of Augugliaro et al. [29].

When the activities are compared in relative terms referenced to Degussa P25, as it is shown in Fig. 3, the activity of the silica-supported materials is always higher for the methanol photooxidation reaction test. This high concentration of methanol has been previously reported to avoid the possibility of the inner transport control in the global kinetics [27], which could not be discarded in cyanide test reactions.

Taking into account that the six supported photocatalysts has been prepared through the same synthesis procedure, they exhibit similar average titania crystal sizes, and the reaction has been carried out with equal titania mass concentration, the expected values for the surface reaction rate with the six materials should be essentially the same. However, the materials supported on SBA-15 always show higher activities than their correspondent $GrSiO_2$-based materials, either in terms of the specific or surface reaction rate, in spite of the diffusional restrictions already suggested for cyanide photooxidation. On the other hand, it seems that the increase in the titania loading leads to higher specific and surface reaction rate values, especially for the materials supported on $GrSiO_2$. Assuming that main properties of the titania crystals of the six materials are very similar, we can consider that the intrinsic kinetics of the oxidation reaction and the electron-hole recombination rate are more or less the same. Consequently, differences in the surface based reaction rates must be caused: (i) by the adsorption step, conditioned by the type of silica support and the SiO_2/TiO_2 ratio or (ii) by a different local volumetric rate of photon absorption. The first point does not

seem to be very plausible due to the high methanol concentrations used in this work. Consequently, differences in the photon absorption step are proposed as responsible for the discrepancy in the surface based reaction rate values.

4. Conclusions

The procedure developed in this work represents an important contribution to the quantification of the activity of supported photocatalysts that will permit the comparison of the results obtained by different research groups with TiO_2/SiO_2 catalytic systems of different nature, such as catalyst suspensions, films or titania deposited on glass tubes.

The results here reported suggest the possibility of achieving surface activity rates even higher than the material Degussa P25 when using nanocrystalline titania supported on silica. TiO_2/SiO_2 materials combine the high activity of titania nanocrystals with the increase in active surface area derived from the homogeneous dispersion on the support.

In photocatalytic processes, the determination of the catalytically active surface area is essential for the rigorous kinetic modelling of the reactions, as the charge transfer processes are considered to take place on the titania–fluid interface. However, although the specific surface area values have been extensively used to justify differences in photocatalytic activity of pure TiO_2 materials, this is the first time that the titania surface of mixed TiO_2/SiO_2 photocatalysts is estimated.

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