New Silica Supported Titanium Dioxide Catalysts: Characteristics and Photocatalytic Efficiency in Waste Water Depollution

Noureddine Kamil[a], Mohamed Khalid El Amrani[b], and Najiba Benjelloun[b]

[a] Ecole Supérieure de Technologie de Casablanca, B.P. 8012, Oasis Casablanca, Morocco
[b] Faculté des Sciences-Aïn Chok, B.P. 5366 Maârif, 20100 Casablanca, Morocco

Reprint requests to N. Kamil. Fax: +212 22 25 22 45. E-mail: kamil@est-uh2c.ac.ma

Silica gel supported titanium dioxide photocatalysts were prepared by sintering TiO_2/SiO_2 mixtures under variations of TiO_2 content, calcination temperature and calcination time. The method allowed to obtain catalyst samples, which can be used in aqueous suspension and which were found to be easily separated by decantation after the photocatalytic treatment. The photocatalytic efficiency of the catalysts was tested by carrying out the photooxidation of the textile dye Acid Red 88 (AR88) in aqueous solution, used as "model" water pollutant. The obtained photoefficiency results were correlated to catalyst physicochemical characteristics, as determined by Inductively Coupled Plasma (ICP) analysis, X-ray diffraction, specific surface area (BET) and scanning electron microscopy (SEM). No positive correlation has been observed between titanium dioxide content and photocatalytic efficiency. The decrease of photocatalytic activity at high calcination temperature (1000 °C) is attributed to the phase transition anatase/rutile as well as to the decreasing specific surface area. According to SEM analysis, no significant fixation of TiO_2 on silica is observed for catalysts prepared at low temperature (400 °C). The observed photocatalytic activity is consequently due to free TiO_2 particles. The best efficiency is observed for photocatalyst prepared at 800 °C and containing around fifty percent titanium dioxide.

Key words: Silica, Titanium Dioxide, Photocatalysis, Depollution

Introduction

Heterogeneous photocatalysis using semiconductor materials, such as titanium dioxide, is one of the emerging Advanced Oxidation Processes (AOP) that has been shown to be effective in destroying a wide variety of organic and inorganic compounds in air and water [1]. These processes can be used also with high efficacy in waste water treatment or purification and are possible alternatives to conventional water treatment technologies [2]. When TiO_2 is illuminated with light near the ultraviolet spectrum, hydroxyl radicals are generated at the surface of the semiconductor and oxidize organic pollutants [3]. In laboratory experiments, near UV light is provided by lamps but in some experimental pilot plants like Plataforma solar of Almeria in Spain, solar light collectors are used for the photoactivation of the catalyst [3].

In most studies of photocatalytic waste water depollution with titanium dioxide (Degussa P25, for example), the photocatalyst is used as an aqueous suspension [4 – 7]. If these catalysts are widely accepted as the most active materials in photocatalysis, the colloidal nature of the fine particles in aqueous media is a major inconvenience for their use in large scale. Thus, the recovery of the catalyst is compromised because the sedimentation of the fine particles is very slow. Post treatment removal requires membrane filtration which adds to the running coasts of the plant. In addition, the turbidity of highly concentrated titanium dioxide suspensions is responsible of a light shadowing effect, which can drastically lower the rate of the photocatalytic reaction. The alternative approach is to immobilize the TiO_2 photocatalyst on the surface of various inert substrates [8 – 10]. Post treatment removal is eliminated but there is a decrease in the surface area, and consequently a decrease in photocatalytic efficiency in addition to optical constraints in the reactor design. Therefore, a photocatalyst allowing high performance and easy recovery after treatment and avoiding the optical limitations of immobilized catalyst configurations is desirable.

Titanium dioxide photocatalysts fixed on fine silica particles are developed in our laboratory [11]. The new

Initial proportion	20% TiO$_2$	80% SiO$_2$	80% TiO$_2$	20% SiO$_2$
Calcination time in hours	4	6	4	6
Calcination temperature: T = 400 °C	C$_1$	C$_2$	C$_5$	C$_6$
Calcination temperature: T = 1000 °C	C$_3$	C$_4$	C$_7$	C$_8$

Table 1. Preparation conditions of series S1.

Initial proportion	20% TiO$_2$	40% TiO$_2$	60% TiO$_2$	80% TiO$_2$
Calcination temperature: T = 800 °C Calcination time: t = 6 h	C$_9$	C$_{10}$	C$_{11}$	C$_{12}$

Table 2. Preparation conditions of series S2.

photocatalyst is used as a suspension in a slurry reactor. It can be easily separated by decantation after the water treatment and directly recycled in a continuous process. Other studies on silica/titania catalysts prepared by the sol gel technique [12] or chemical vapour deposition [13] showed that these catalysts may be more or less photoactive than currently used titanium dioxide. The photocatalytic activity of TiO$_2$/SiO$_2$ catalysts is related to the preparation process, the allotropic crystal form, the presence of impurities and the specific surface area.

The purpose of this study is the correlation between the physicochemical characteristics and the photocatalytic activity of new catalysts obtained by supporting TiO$_2$ on finely suspended particles of silica powder. Series of TiO$_2$/SiO$_2$ catalysts were prepared by sintering under conditions to investigate the effect of their properties on photocatalytic efficiency. The new catalysts were tested by carrying out the photodegradation of the textile dye AR88 used as "model" pollutant. Characterization of the catalysts includes ICP analysis, X-ray diffraction, specific surface area determination (BET) and scanning electron microscopy (SEM).

Experimental Section

The products used are: TiO$_2$ anatase (Farmitalia) and SiO$_2$ silica gel (Merck). Photocatalysts were prepared by sintering mixtures of titanium dioxide and silica gel. The preparation of these photocatalysts is realized according to the proceedings described in a patent deposited by our laboratory [11]. The relevant preparation factors are the amount of titanium dioxide, the calcination temperature and the calcination time. TiO$_2$ content was varied from 20 to 80%, calcination temperature from 400 to 1000 °C and calcination time from 4 to 6 h. Two series of catalysts S1 and S2 were prepared under the conditions summarized respectively in Tables 1 and 2.

Chemical analysis of catalyst samples was performed by ICP analysis (Atomic emission spectrometer ICP JY 70). Photocatalytic experiments were performed in a photochemical reactor with a high pressure mercury lamp (HPK 125 W – Philips), jacketed with a Pyrex filter to cut off UV-light

shorter than 290 nm. The commercial textile dye Acid Red 88 (AR88) (4-(2-hydroxy-1-naphthylazo)-1-naphthalenesulfonic acid, sodium salt) was used without further purification.

A suspension containing 0.5 g/l of catalyst and 300 ml of 10 ppm AR88 solution was stirred continuously in the dark for more than 1 h to achieve the adsorption equilibrium on the surface of the catalyst. At given intervals of irradiation, small aliquots of the suspension were withdrawn, filtered through a Millipore filter and analyzed by UV-visible spectroscopy (Secomam-Anthelie-Data-Onascu Spectrophotometer) at 510 nm, which is the maximum absorption wavelength of AR88. The half reaction times of photodegradation for the different catalysts were determined from kinetic profiles.

Crystalline phases of catalyst samples were determined by X-ray diffraction. The patterns were recorded on X'Pert MPD diffractometer by using Cu-K$_\alpha$ radiation. Diffraction patterns were taken over the 2θ range (5 – 60°). The BET specific surface area was determined by nitrogen physisorption data at 77 K using Gemini 2360V500, ID Instrument. The morphology of aggregated particles was observed by scanning electron microscopy (XL 30 ESEM).

Results and Discussion

Chemical analysis of the catalysts

The first parameter considered in this study is the determination of chemical composition of the catalysts after preparation. Table 3 presents the contents in weight % of TiO$_2$ and SiO$_2$ determined by ICP analysis.

The obtained contents approach the initial concentrations. Differences are explained by a loss of TiO$_2$ and SiO$_2$ fine particles during the last washing step as described in the preparation procedure [11].

Photoactivity of TiO$_2$/SiO$_2$ photocatalysts

In all heterogeneous catalytic regimes, the initial reaction rate was found to be directly proportional to the effective mass of the catalyst with an optimum, which depends on the geometry of the photoreactor and the

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
%TiO$_2$	22.92	19.6	25.2	24.95	74.95	82.31	85.03	83.42	18.9	28.12	51.93	75.97
%SiO$_2$	75.67	80.58	70.00	77.67	26.06	17.17	15.74	17.63	79.73	71.13	47.54	22.40

Table 3. Catalyst compositions.

Table 4a. Half reaction-times with TiO$_2$/SiO$_2$ catalysts, series S1.

Catalyst	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
% TiO$_2$	23	20	25	25	75	82	85	83
t$_{1/2}$ (min)	55	54	84	105	46	62	76	153

Table 4b. Half reaction-times with TiO$_2$/SiO$_2$ catalysts, series S2.

Catalyst	C_9	C_{10}	C_{11}	C_{12}
% TiO$_2$	19	28	52	76
t$_{1/2}$ (min)	83	61	40	55

Table 5a. BET Analysis for samples C_1 to C_8.

Series 1	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
B.E.T in m^2/g	171	180	1	2	114	96	2	2

Table 5b. BET Analysis for samples C_9 to C_{12}.

Series 2	C_9	C_{10}	C_{11}	C_{12}
B.E.T in m^2/g	70	141	160	134
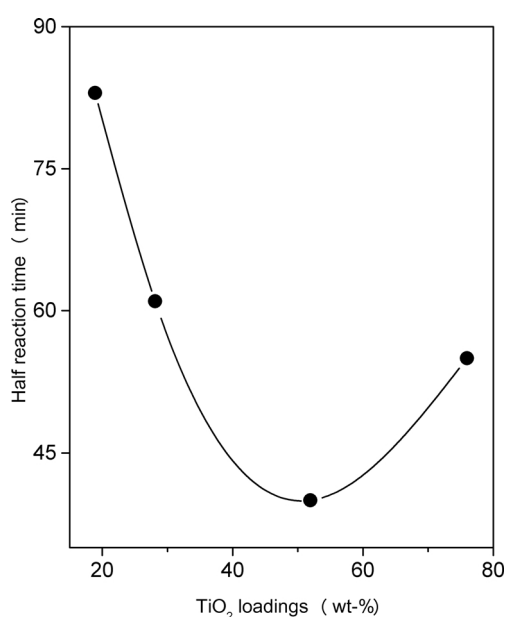
Fig. 1. Effect of TiO$_2$ loading on photoefficiency of TiO$_2$/SiO$_2$ catalysts prepared at 800 °C for 6 h.

operating conditions. Preliminary experiments in our laboratory, using the same photoreactor and the same operating conditions as in this study, have given an optimum of catalyst concentration of 1.5 g/l. Nevertheless, the chosen catalyst concentration in this work is 0.5 g/l, which is large enough to compare the photoactivities of the prepared catalysts. Tables 4a and 4b show the half-reaction times t$_{1/2}$ corresponding to the photodegradation of AR88 in presence of the two series of photocatalysts C_1 to C_8 and C_9 to C_{12}, respectively.

According to a global analysis of these results, we can note that high TiO$_2$ loading in the samples does not necessarily enhance photocatalyst efficiency. There is no positive correlation between TiO$_2$ content and photocatalytic activity, despite of the fact that titanium dioxide is the catalytic agent and SiO$_2$ is only the inert support.

In the first series, calcination temperature is the mean determinant factor affecting the photoactivity. At high calcination temperature, photocatalyst activity decreases. Calcination time is not significant at 400 °C, but this parameter has a negative effect on the efficiency of the catalyst at 1000 °C and this effect is enhanced with high TiO$_2$ loading.

In the second series, we study only the effect of TiO$_2$ loading. All of the samples C_9 to C_{12} are prepared under the same conditions with a calcination temperature of 800 °C and a time of calcination of 6 h. The effect of the TiO$_2$ loading on the photoefficiency of TiO$_2$/SiO$_2$ particles is shown in Fig. 1. The minimum half reaction time is observed around 50% TiO$_2$.

Characterization of TiO$_2$/SiO$_2$ photocatalysts

BET specific surface area of titania/silica catalysts prepared at 400 °C and 1000 °C for the catalysts C_1 to C_8 and at 800 °C for the catalysts C_9 to C_{12} are presented in Tables 5a and 5b, respectively. Specific surface area is very low at 1000 °C (C_3, C_4, C_7 and C_8). The highest specific surface area is observed for C_1 and C_2 prepared at 400 °C. These results are in agreement with photocatalytic activity results presented in Table 4a, and show that catalyst photoactivity is enhanced with increasing specific surface area. In the second series of catalysts prepared at 800 °C, all the samples show high specific surface area. The highest value is obtained for the catalyst C_{11}, which is the most photoactive catalyst.

The effect of TiO$_2$ loading on BET surface area for series 2 catalysts is shown in Fig. 2. The presence of
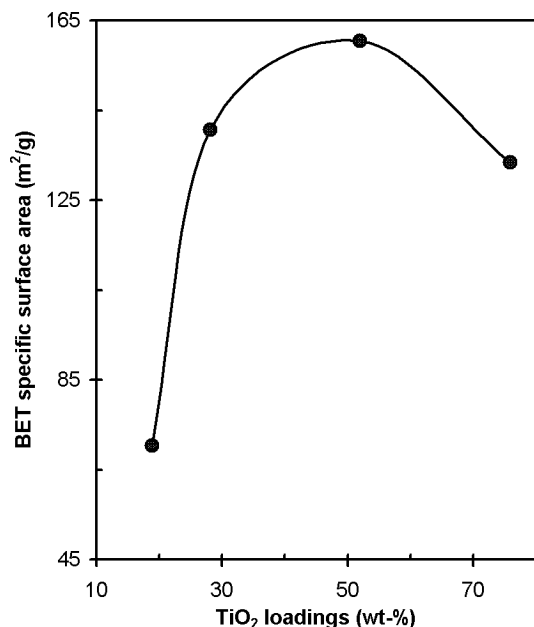
Fig. 2. BET specific surface area for catalysts prepared at 800 °C as a function of TiO_2 loading.

crystalline phases in samples C_1 to C_{12} was determined by X-ray diffraction analysis. Figs. 3, 4 and 5 show the XRD patterns of TiO_2/SiO_2 catalysts at different calcination temperatures according to the two series S1 and S2. For series S1, two types of patterns are observed. In Fig. 3, for the catalysts prepared at 400 °C (C_1, C_2, C_5, and C_6), only pure anatase phase is ob-

served. The peaks corresponding to this phase appear at $2\theta = 25.3$, 38, 48.2, and 54°. On the other hand, three crystalline phases: anatase, rutile and cristobalite are observed for the catalysts C_3, C_4, C_7, and C_8 prepared at 1000 °C (Fig. 4). The peaks corresponding to the rutile phase appear at $2\theta = 27.4$, 36.2, 39.5, 54.4, 56.9°, and the peaks corresponding to the anatase phase are conserved. In addition, the peaks corresponding to the cristobalite phase appear at $2\theta = 22.0$, 25.3, 31.4°. As shown in Fig. 4, a part of TiO_2 was transformed from the anatase to the rutile phase and at least a part of amorphous SiO_2 was transformed to crystalline phase. For series S2, corresponding to the catalysts C_9 to C_{12} prepared at 800 °C, the observed phase is pure anatase (Fig. 5). Silica particles remain in the amorphous state.

The morphology of titania/silica catalysts was observed by scanning electron microscopy. Fig. 6 presents the SEM micrograph of catalyst sample C_1 prepared at 400 °C. We can observe a dispersion of fine primary particles without any fixation of titania on silica. When the calcination temperature increases from 400 °C to 1000 °C, we observe a significant particle aggregation as shown in Fig. 7. In this example, silica particles are completely covered by large titania aggregates. Fig. 8 is a SEM micrograph of one sample from the second catalysts series prepared at 800 °C. In this case, we observe dispersion and fixation of titania particles on silica. Analysis of all the samples prepared at
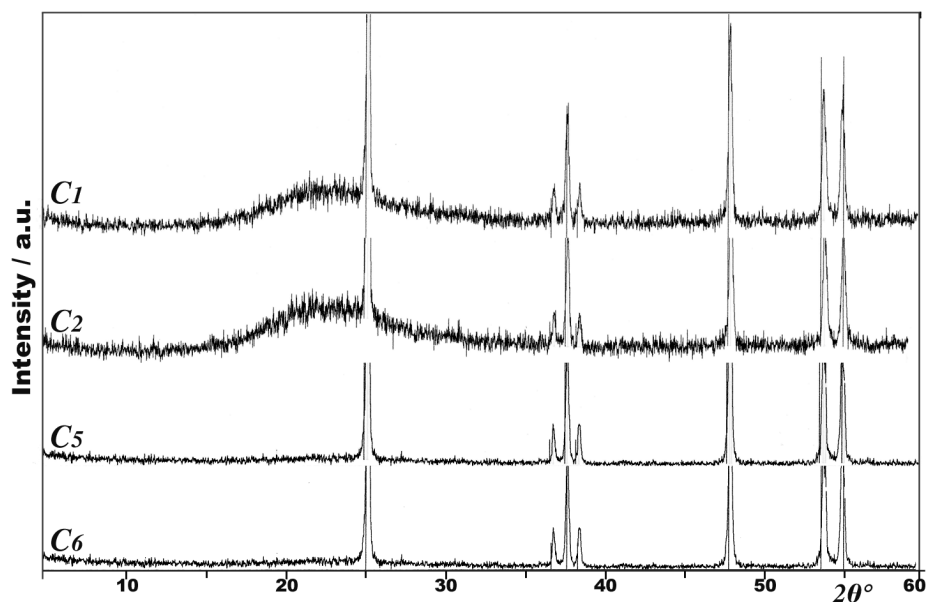

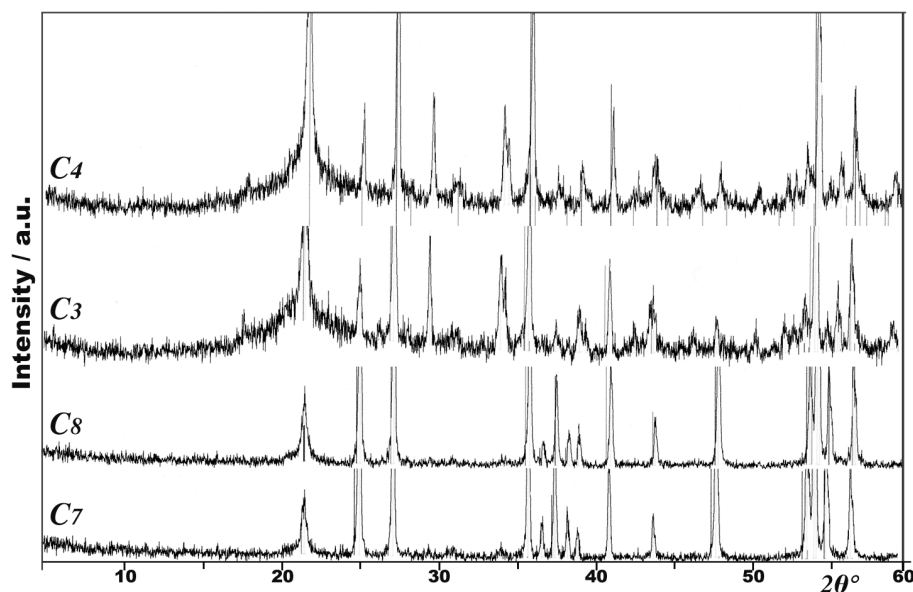Fig. 3. XRD patterns of samples calcined at 400 °C.

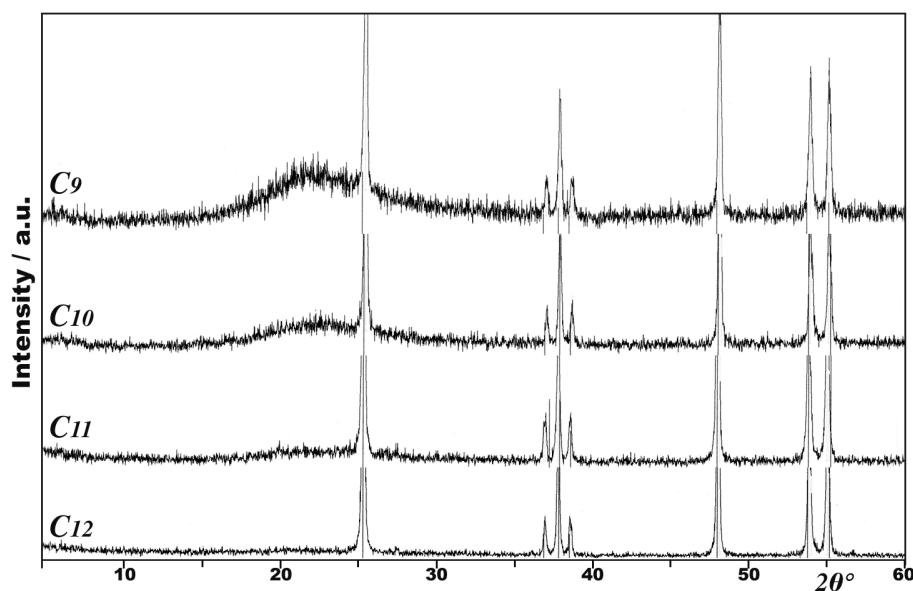Fig. 4. XRD patterns of samples calcined at 1000 °C.

Fig. 5. XRD patterns of samples calcined at 800 °C.

800 °C shows that fixation of titania particles was increased with increasing TiO_2 content. The phenomenon is however less important than for the samples prepared at 1000 °C.

Discussion

The aim of this work was to explain the photocatalytic efficiency of our catalysts prepared by sintering, in relation with titanium dioxide and silica crystalline phases present in the sample, its titanium dioxide loading and its specific surface area. All results of this study are summarized in Tables 6a and 6b. Photocatalysis results combined with XRD, BET and SEM analyses of series S1 catalysts show two distinct phenomena depending on calcination temperature. There is no fixation of titanium dioxide on silica and no crystalline phase change at 400 °C. This temperature is too low to change anything in the structure of titania and silica particles. Consequently, calcination times do not
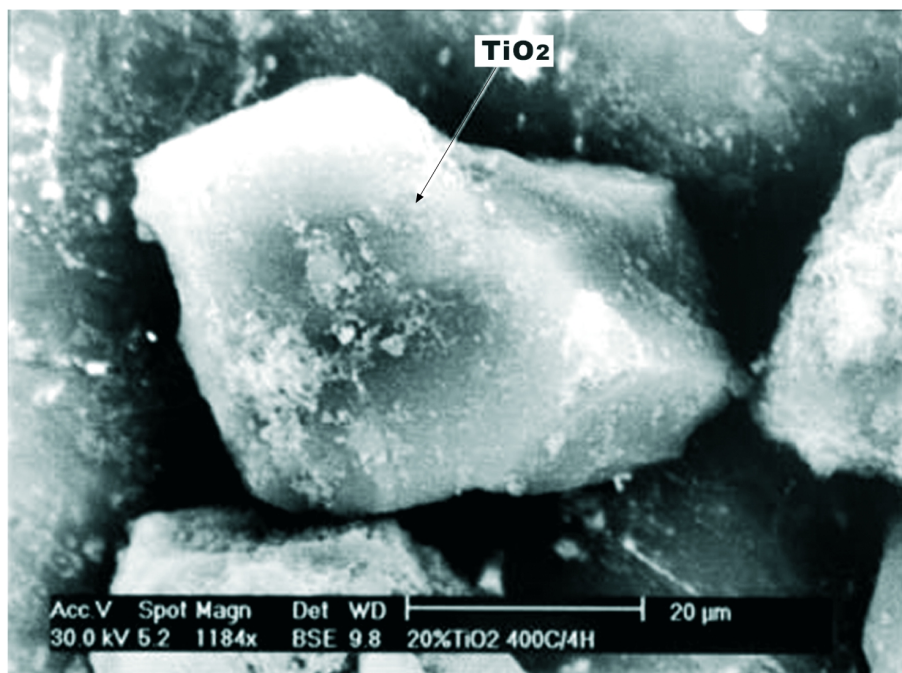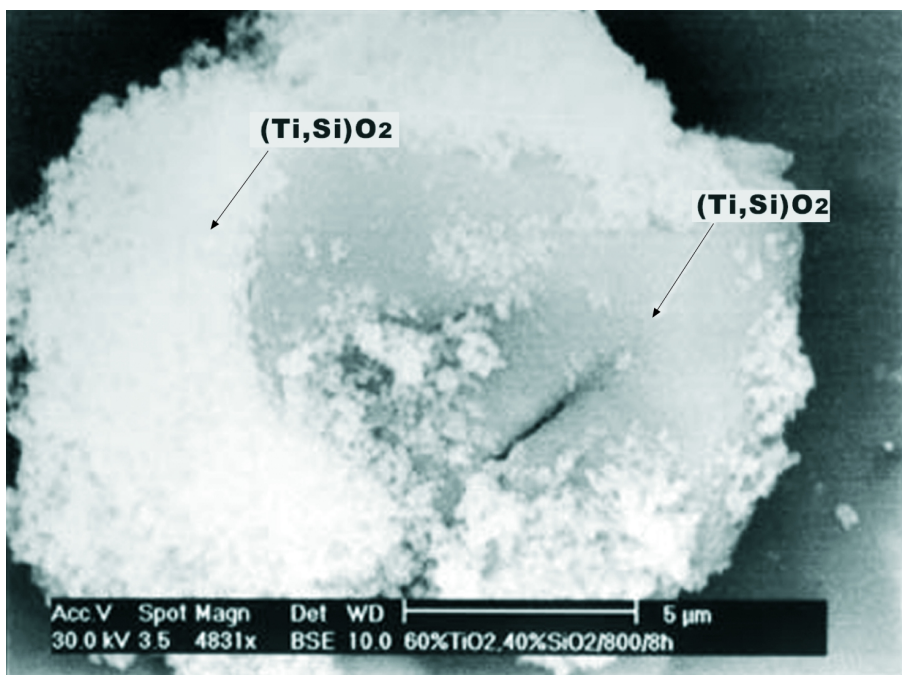
Fig. 6. SEM micrograph of the sample C_1.

Fig. 7. SEM micrograph of the sample C_7.

have any effect on photocatalytic efficiency. The observed photocatalytic activity is probably only due to free primary particles of titanium dioxide dispersed on silica.

Moreover, the obtained specific surface area is nearly the average of the specific surface area of the initial particles. In another way, catalyst samples prepared at 400 °C do not present the required stability
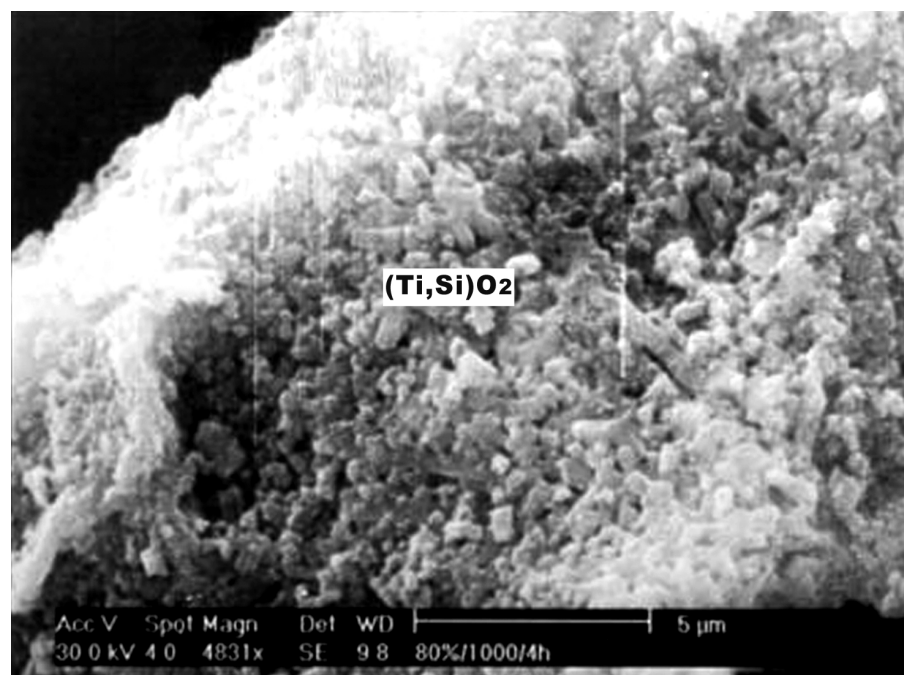
Fig. 8. SEM micrograph of the sample C_{11}.

Table 6a. Results of series S1.

Catalyst	% TiO_2	$t_{1/2}$min	BET m^2/g	Phases	TiO_2 Fixation
C_1	23	55	171	anatase	no
C_2	20	54	180	anatase	no
C_3	25	84	1	anatase, rutile, cristobalite	agglomeration
C_4	25	105	2	anatase, rutile, cristobalite	agglomeration
C_5	75	46	114	anatase	no
C_6	82	62	96	anatase	no
C_7	85	76	2	anatase, rutile, cristobalite	agglomeration
C_8	83	153	2	anatase, rutile, cristobalite	agglomeration

Table 6b. Results of series S2.

Catalyst	% TiO_2	$t_{1/2}$min	BET m^2/g	Phases	TiO_2 Fixation
C_9	19	83	70	anatase	good
C_{10}	28	60	141	anatase	good
C_{11}	52	40	160	anatase	good
C_{12}	76	55	134	anatase	good

in aqueous media. The obtained suspensions are colloidal and are therefore not easily decantable, which may compromise their reuse in a continuous process.

At 1000 °C, two phase transitions are observed, silica gel to cristobalite and titania anatase to rutile form. Similar results have been reported by Gouma *et al.* for commercial titanium dioxide [14]. On the other hand, SEM micrographs show significant agglomeration of particles, which is enhanced by longer calcinations times. The low photoactivity of these catalysts could be explained by the presence of large amounts of rutile form and the very important decrease of the specific surface area.

For the series S2 catalysts prepared at 800 °C, we do not observe any phase change whatever is the catalyst composition. Nevertheless, the fixation of TiO_2 anatase on amorphous silica particles is confirmed by SEM results. All these catalysts have large specific surface areas with a maximum for the catalyst C_{11} corresponding to a TiO_2 content of nearly 50%. Consequently, the photodegradation tests of AR88 give an activity maximum for the same catalyst. This behaviour could be explained by the effect of amorphous silica, which probably increases the thermal stability of titania anatase form and makes it therefore possible to sinter the silica/titania particles at higher calcination temperature. The same conclusion has been reached by other authors for TiO_2/SiO_2 prepared by sol gel technique at 700 °C [12] or by chemical vapour deposition at 500 °C [13]. Furthermore, the presence of amorphous silica seems to avoid the reduction of specific surface area, which is generally observed at high calcination temperatures.

Conclusion

Low photoactivity of catalysts prepared at 1000 ℃ is mainly due to the very significant decrease of specific surface area as well as phase transitions of titania anatase to rutile form and silica gel to cristobalite. At 800 ℃, the fixation of titania on silica particles increases without any phase change. High specific surface area and high photocatalytic performances are therefore obtained. Moreover, there is no direct correlation between TiO_2 content and photocatalytic activity despite of the fact that titanium dioxide is the real catalytic agent and SiO_2 is just the inert support. The best photocatalytic properties are obtained at 800 ℃ for a TiO_2 content near 50%.

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