Research Article

Photocatalytic Activity in CH₃CN Related to the Surface Properties of TiO₂ Powders Prepared by Sol-Gel Method

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Some TiO₂ powders, prepared from titanium(IV)tetraisopropoxide by the sol-gel method and thermally treated between 100 and 1000°C, have been characterized by X-ray powder diffraction and by nitrogen adsorption and desorption at 77 K to calculate the BET-specific surface area, from which the micropore volume and the external surface area can be derived. The photocatalytic activity (k_a) of the above powders has been evaluated considering the TiO₂-sensitized photo-oxidation of 4-methoxybenzyl alcohol in CH₃CN as the test reaction. The decrease of k_a have been related to the decrease of the BET surface area, the micropore volume, and the external surface area of the TiO₂ powders, but a satisfactory linear correlation is observed only for the last superficial parameter.

1. Introduction

Heterogeneous photochemical processes sensitized by semiconductors, such as TiO₂, have gained wide popularity because of their application, mainly to water or atmosphere detoxification, to conversion or storage of solar light energy, and to synthetic or mechanistic organic chemistry [1, 2].

Photo-oxidation reactions of organic compounds sensitized by TiO₂ in CH₃CN have been studied also from the point of view of their reaction mechanism because this reaction medium is suitable to dissolve the organic substrates and is not competitively oxidizable. Moreover, the primary oxidation products usually are not furtherly degraded, allowing material recovery (unreacted substrate + formed product) and stoichiometry to be evaluated. The primary oxidation products are generally obtained through an electron transfer mechanism between the photogenerated hole, $(TiO_2)_{h^+}$, and the substrate, giving a radical cation as intermediate [3].

In recent years, many mechanistic details have been collected about this TiO₂-sensitized oxidative process on benzylic derivatives (arenes [4], alcohols [5–7], ethers [8], silanes [7], sulfides [9–11], diols [6, 12] etc.) in CH₃CN. In these works only TiO₂ commercial powders have been considered (anatase, Aldrich, or P25, Degussa).

In this paper we report the results of a study that allow a correlation of the photochemical activity in CH₃CN to the superficial texture and the crystal form of different synthetic TiO₂ powders. These photocatalysts were prepared by a sol-gel method starting from titanium isopropoxide, calcined at different temperatures (100–1000°C for one hour) and characterized by X-ray diffraction (XRD) and by nitrogen adsorption and desorption at 77 K.

In this context, it has been previously reported that powders, prepared though the sol-gel method in the absence of any kind of additives and calcined at different temperatures, show different photochemical efficiencies in the photo-oxidations of appropriate test samples, either in water and in gas phase [13–16].

In this work, the photocatalytic activity of the powders have been evaluated through the photo-oxidation in CH₃CN of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde, a reaction of known stoichiometry and mechanism [7, 17, 18].

2. Experiments

2.1. Materials. Titanium(IV)tetraisopropoxide (TTIP, Aldrich, 97%), TiO_2 (P25, Degussa), isopropanol (IP, Carlo Erba, 99.7%), CH_3CN (99.9%, HPLC grade, containing 0.02% of water from Karl Fisher analysis), and 4-methoxybenzyl alcohol (Aldrich, 98%) were commercial samples.

2.2. Preparation of TiO_2 Powder. For the synthesis of the TiO_2 powder, TTIP (12 mL) was added to 500 mL of IP with constant magnetic stirring at room temperature. Milli-Q water (2500 mL) was then added slowly to the solution. The obtained mixture (TTIP : IP : H_2O molar ratio = 1 : 3 : 240) was vigorously stirred for 24 hours in a closed flask. The fine white precipitate dispersed in the solvent was filtered and washed with Milli-Q water. The white residue was dried in oven at 100°C for 24 hours and then it was grinded by a ceramic mortar. The derived particles were thermally treated for 1 hour at 200, 300, 350, 400, 500, 700, 850, and 1000°C.

2.3. Characterization of TiO_2 Powders. X-ray powder diffraction (XRD) analyses were performed on a computerized Philips PW1710 diffractometer using Cu Kα radiation, operating at 40 kV and 20 mA with a step scan of 1°C/min.

Nitrogen adsorption/desorption isotherms at 77 K were measured using a computer-controlled Micrometrics ASAP 2010 adsorption analyzer. The preparation of samples was made by degassing the materials at 100°C, overnight. The specific surface area was calculated by the Brunauer, Emmett and Teller (BET) theory. Micropore volume and external surface area of the catalysts were obtained by application of the *t*-plot method [19]. The Harkins-Jura equation was used as reference for the thickness of the adsorbed layer [19].

The thermogravimetric analysis of the sample dried at 100°C, stored at room temperature, 75% r.h., was performed with a Netzsch STA 449C thermobalance with a temperature gradient of 5°C/min.

2.4. Photochemical Oxidation. A solution of the substrate (1.0×10^{-2} M) in 10 mL of CH_3CN, containing 10 mg of TiO_2, was externally irradiated using a Helios Italquartz 500 W high pressure mercury lamp (through Pyrex filter), under stirring at room temperature. In the present work, we are mainly interested to the relative photocatalytic activity of powders and therefore we did not measure the irradiation intensity. However, for such a lamp, one typically expects a photon flux emission between 15 and 20 mW cm^{-2}. After irradiation, the reaction mixture was filtered through double paper and analyzed by gas-chromatography (GC, in the presence of bibenzyl as internal standard). The GC analyses were carried out on a HP 5890 gas-chromatograph using a HP-Innovax capillary column, 15 m.

3. Results and Discussion

3.1. Powders Synthesis. The TiO_2 powders were prepared by hydrolysis of TTIP in IP and subsequent calcination at 100
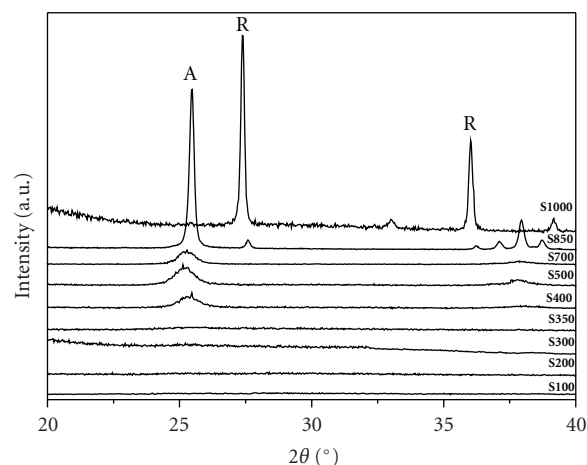

Figure 1: XRD patterns of the indicated samples.

(denoted as **S100**), 200 (**S200**), 300 (**S300**), 350 (**S350**), 400 (**S400**), 500 (**S500**), 700 (**S700**), 850 (**S850**) and 1000°C (**S1000**).

3.2. X-Ray Diffraction. XRD patterns of the samples **S100-S1000** are shown in Figure 1. Diffraction maxima due to the anatase form of TiO_2 were evident after thermal treatments from 400 to 700°C (**S400**, **S500**, and **S700** samples). A further increase of calcination temperature brings to the appearance of the rutile crystalline form besides that of anatase (**S850**). In the case of **S1000** sample, only maxima ascribed to the rutile crystalline form are observed. From XRD results the **S100-S350** samples do not present any evident christallinity, but TEM measurements [14, 15] on samples prepared by a similar procedure and calcined at temperatures from 100 to 300°C evidentiate aggregates of fine particles.

3.3. Nitrogen Adsorption-Desorption Isotherms. Surface area and porosity of obtained solids were calculated by nitrogen adsorption and desorption at 77 K. Some of these isotherms are shown in Figure 2.

The adsorption-desorption isotherm of **S350** is similar and superimposed to all the samples below 350°C (**S100, S200,** and **S300**) and can be classified as type II isotherm.

Increasing the temperature of the thermal treatment from 350 to 1000°C, the adsorption isotherm gradually changes from type II to type III.

The little hysteresis present between the desorption and adsorption isotherms of some samples, in the range $0.4 < p/p_0 < 0.6$, indicates that a little volume of mesopores is present.

The BET adsorption analysis data allows to calculate, for the various samples, the specific BET surface area. This area depends on the temperature of the thermal treatment: higher values of surface area are measured for the samples treated at temperatures lower than 350°C (see Figure 3).

Increasing the thermal treatment temperatures above 350°C, BET surface area diminishes until a very low value at 1000°C (**S1000** sample). The decrease of BET
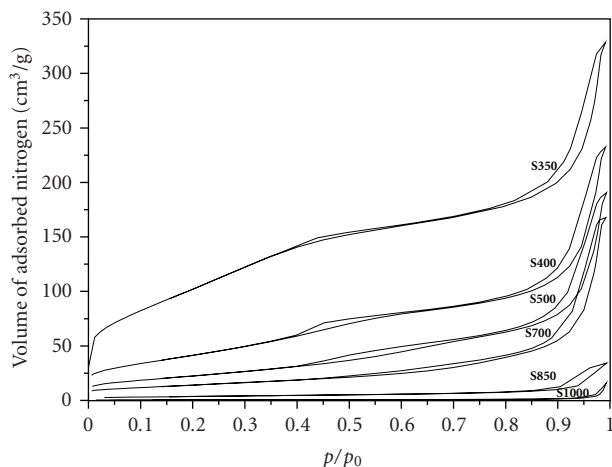
Figure 2: The nitrogen adsorption-desorption isotherms of the indicated samples.
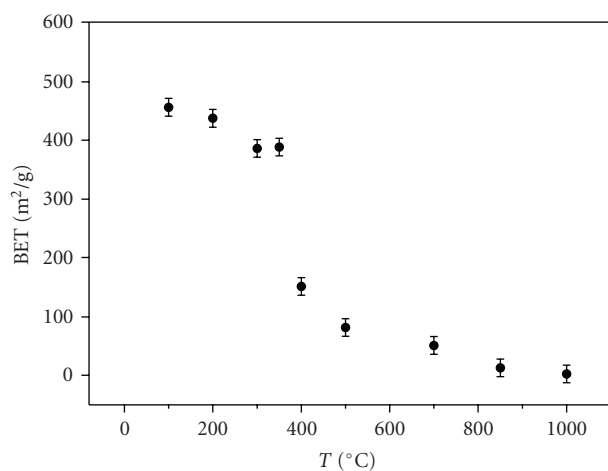

Figure 4: Micropore volume ($\blacksquare$) versus temperature of the thermal treatment of the samples.

Figure 3: BET surface area versus temperature of the thermal treatment of the samples.
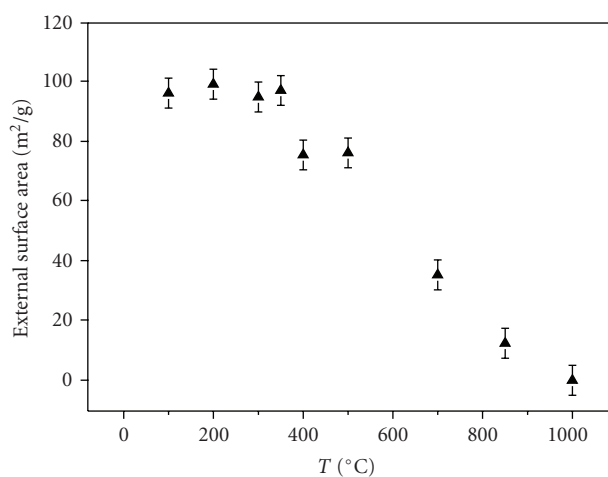
Figure 5: External surface area ($\blacktriangle$) versus temperature of the thermal treatment of the samples.

area (with the enhancement of the calcination temperature) could be related to the increase of crystallinity of the samples [20].

The t-plot analysis of samples adsorption data permits to evaluate the micropore volumes and the external surface area of the samples [19].

The calculated micropore volumes and the external surface area for the prepared samples are plotted against thermal treatment temperature in Figures 4 and 5.

Samples with a micropore volume higher than 0.18 cm^3/g were obtained when the temperature of the thermal treatment do not exceed 350°C. The increase of the temperature above 350°C induces a decrease in the micropore volume and in the external surface area. This is consistent with the increase of the crystallinity of the samples.

The micropore size distribution calculated by the MP method [19] is narrow; for example, the hydraulic radius relative to the powder **S350** is in the range 5–8 angstrom.
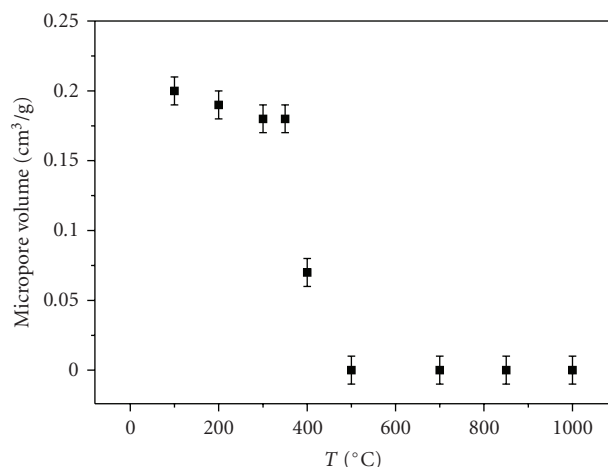
3.4. Photocatalytic Activity. As it has been mentioned in the Introduction, in order to evaluate the photocatalytic activity of the different TiO$_2$ powders, we have considered a photo-oxidation test reaction in liquid phase previously extensively studied by us, that is, the TiO$_2$ photosensitized oxidation of 4-methoxybenzyl alcohol in CH$_3$CN (1):

$$H_3CO-\!\!\!\bigcirc\!\!\!-CH_2OH \xrightarrow[\text{CH}_3\text{CN}]{\text{TiO}_2,\,h\nu} H_3CO-\!\!\!\bigcirc\!\!\!-CHO$$

$$(1)$$
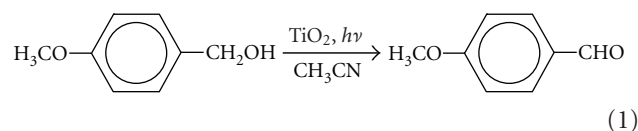
The recognized reaction mechanism and, consequently, the reaction stoichiometry, are reported in Scheme 1.

$$\text{TiO}_2 \xrightarrow{h\nu} (\text{TiO}_2)_{h^+} + (\text{TiO}_2)_{e^-} \qquad (2)$$
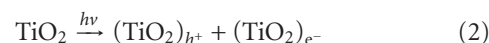
The aldehyde conversions, obtained at different times in the presence of TiO$_2$ powders thermally treated from 100
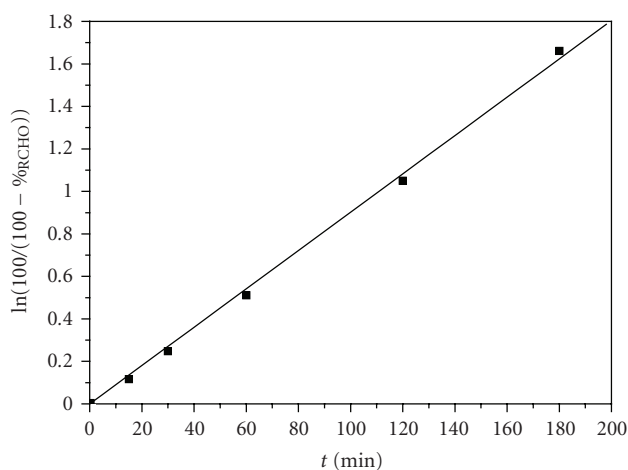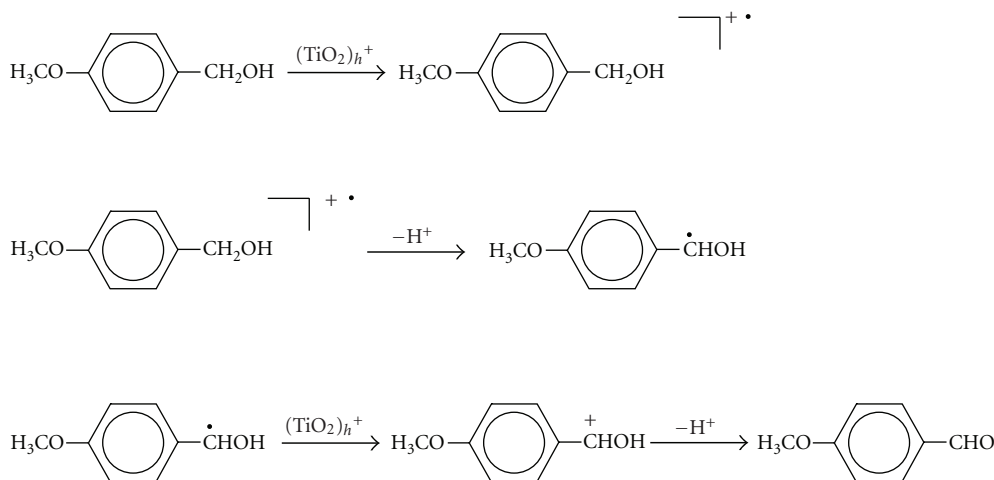
SCHEME 1

FIGURE 6: Kinetic plot relative to the photo-oxidation in the presence of **S200** sample.

to 1000°C, are reported in Table 1. In the same table are also reported the data relative to the commercial TiO_2 P25 powder.

The photocatalytic activity of the different powders can be quantitatively evaluated by the apparent rate constants (k_a) calculated by the following Langmuir-Hinshelwood rate expression:

$$\ln[100/(100 - \%_{RCHO})] = k\,K\,t = k_a\,t, \tag{3}$$

where $\%_{RCHO}$ is the aldehyde percent at the various times (t), k is the true rate constant and K is the substrate adsorption constant on TiO_2. As an example, the linear plot $\ln[100/(100 - \%_{RCHO})]$ versus t ($r = 0.994$), relative to the photo-oxidation in the presence of the sample **S200,** is reported in Figure 6.

All k_a values are reported in Table 1. From these kinetic data it can be observed that the samples **S200, S300**, and **S350** are the most photochemically efficient (k_a in the range 9–10× 10^{-3} min^{-1}). Samples **S100, S400, S500, S700,** and **S850** are

less efficient ($k_a = 4$–7×10^{-3} min^{-1}). Finally, the sample **S1000** is the least reactive one ($k_a = 0.3 \times 10^{-3}$ min^{-1}), mostly due to its crystal form (rutile, less efficient than anatase) [21].

A further point to be considered is that all prepared photocatalytic powders (exept **S1000**) are more efficient than the commercial photocatalyst P25 (see Table 1).

Moreover, no reaction takes place in the absence of light or in the absence of catalyst until the considered reaction time (3 hours).

It must be observed that the sample **S100** presents a great water amount (*ca* 13% w/w, from thermogravimetric analysis) that could reduce the sites available to the substrate adsorption and then the k_a value; therefore, we have not thought it convenient to consider this sample in the following discussion.
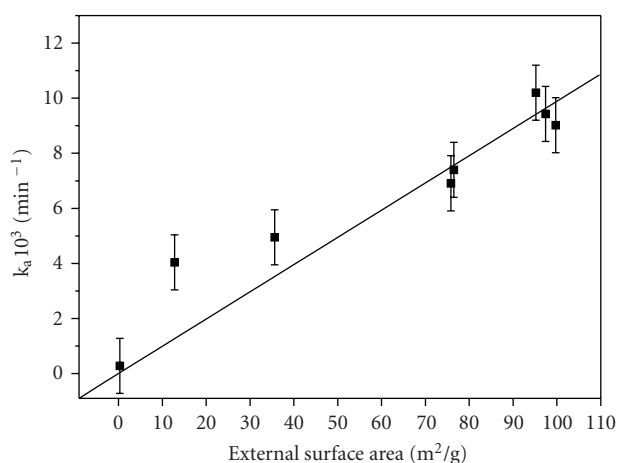
Therefore, considering only the k_a values relative to **S200-S1000** samples in Table 1 and their calcination temperature, a rate decrease when the temperature increases is qualitatively observed.

As the test reaction occurs at the interface between the solid photocatalyst and the organic solution, it is expected that the observed relationship should be connected with the solid-solution interface characteristics and, in particular, to the superficial properties of TiO_2. The above reported characterization of the photocatalyst surface indicates that the BET surface area, the micropore volume and the external surface area depend on the temperature of the thermal treatment: they decrease together according to the trends reported in Figures 3, 4, and 5. Therefore, it seems to be of interest to directly evaluate the relationship between these parameters and k_a.

From the N_2 adsorption data, the calculation of the nitrogen volume which forms a monolayer of adsorbed molecules, and thus the BET surface area value, involves the volume of the nitrogen molecules adsorbed in the micropores and on the external surface area [19]; therefore, the micropore volume and the external surface area are separately taken into account to find a dependence from the measured k_a value.

TABLE 1: Aldehyde conversion and photocatalytic activity (k_a) data obtained in the photo-oxidation with TiO_2 powders.

Sample	Aldehyde yield (%)					$10^3 k_a$ (min^{-1})
	t = 15 minutes	t = 30 minutes	t = 60 minutes	t = 120 minutes	t = 180 minutes	
S100	12	22	35	52	67	6.3
S200	11	22	40	65	81	9.0
S300	20	33	52	77	80	10.2
S350	18	28	43	69	81	9.4
S400	15	26	36	59	69	6.9
S500	14	23	37	57	74	7.4
S700	11	16	27	44	59	4.9
S850	12	17	26	35	57	4.0
S1000	—	1	2	2	6	0.3
P25	14	20	24	33	38	3.1

FIGURE 7: The relationship between external surface area and k_a.

Plotting k_a versus external surface area, a satisfactory linear correlation (r = 0.960) was obtained (Figure 7) while a lower correlation factor (r = 0.777) for k_a versus micropore volume was calculated. Thus, the photochemical activity directly depends from external surface area of the sample, while the micropore volume is less important.

The fact that the photocatalytic activity becomes weaker when the external surface area decreases, could be related to the decrease of the number of OH groups, necessary for the adsorption of substrate at the semiconductor surface, interfaced to CH_3CN [22, 23].

4. Conclusion

The photochemical activity of TiO_2 powders, obtained by a sol-gel method and calcined at different temperatures, has been evaluated through a test reaction (4-methoxybenzyl alcohol → 4-methoxybenzaldehyde) in CH_3CN. In this medium, the increase of calcination temperature induces, on one side, a decrease of BET surface area, of micropore volume and of external surface area and, on the other side, a decrease of the photo-oxidation rate of test reaction. Among the above surface parameters, the one that shows the best linear correlation with the reaction rate is the external surface area.

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