DOI: 10.1002/adsc.200600435

Photocatalytic Selective Oxidation of 4-Methoxybenzyl Alcohol to Aldehyde in Aqueous Suspension of Home-Prepared Titanium Dioxide Catalyst

Giovanni Palmisano,[a] Sedat Yurdakal,[b] Vincenzo Augugliaro,[a] Vittorio Loddo,[a] and Leonardo Palmisano[a],*

[a] Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy
Fax: (+39)-091-656-7280; e-mail: palmisano@dicpm.unipa.it
[b] Kimya Bölümü, Fen Fakültesi, Anadolu Üniversitesi, Yunus Emre Kampüsü, 26470 Eskişehir, Turkey

Received: August 25, 2006

Dedicated to the memory of Prof. Maria Domenica Grillone, who devoted her life to chemistry and her students.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: The photocatalytic oxidation of 4-methoxybenzyl alcohol to *p*-anisaldehyde (PAA) was performed in water with organic-free suspensions of home-prepared and commercial titanium dioxide (TiO_2) catalysts. The nanostructured TiO_2 samples were synthesised by boiling aqueous solutions of titanium tetrachloride ($TiCl_4$), under mild conditions, for different times. The crystallinity increased with the boiling time. The 4-methoxybenzyl alcohol oxidation rate followed the same pattern but the highest yield (41.5% mol) to PAA was found for the least crystalline sample, that showed a quantum efficiency of 0.116%. A comparison with two commercial TiO_2 samples showed that all the home-prepared catalysts exhibited a PAA yield higher than that of commercial ones. The only by-products present were traces of 4-methoxybenzoic acid and aliphatic products, carbon dioxide being the other main oxidation product.

Keywords: *p*-anisaldehyde production; photocatalysis; selective oxidation; titanium dioxide

Introduction

The selective oxidation of alcohols to carbonyl compounds is a process of great industrial importance; generally it is carried out in environmentally harmful organic solvents at high temperature and pressure by employing stoichiometric oxygen donors (such as chromate and permanganate) that not only are expensive and toxic compounds but also produce high amounts of dangerous wastes.[1–5] To overcome these drawbacks, a major goal of chemistry research during the last decade has been that of developing clean catalytic processes with high conversion and selectivity and also using innocuous solvents such as water and supercritical CO_2 for safety and environmental reasons.

For the selective oxidation of alcohols in water a soluble palladium(II) bathophenanthroline complex was used as catalyst at a pressure of 30 bar and a temperature of 373.16 K.[1] The conversion was almost complete and the yield was in the 79–90% range depending on the substrate, but no oxidation of disubstituted aromatic substrates was reported.

Recently Enache et al.[3] reported the oxidation of various alcohols by means of Au-Pd/TiO_2 catalysts: in the case of the oxidation of benzyl alcohol to benzaldehyde the achieved conversion was 74.5% and the selectivity 91.6%, benzyl benzoate being the only detected by-product.

Heterogeneous photocatalysis has been also used for performing selective oxidations. Hydrocarbons were oxidised in aqueous TiO_2 suspensions to obtain alcohols and carbonyl compounds in the presence of artificial irradiation,[6] whereas sunlight induced functionalisation of some heterocyclic bases in the presence of polycrystalline TiO_2 in water/acetonitrile solvents.[7] Selective oxidation of alcohols to the corresponding aldehydes and ketones was performed either in the gas phase[8] or in the liquid phase using acetonitrile as solvent,[9,10] in some cases affording high yields. Remarkably, attempts at performing the selective photocatalytic oxidation of alcohols to aldehydes in organic-free water are not reported in the literature, to the best of our knowledge.

This investigation has been devoted to studying the production of 4-methoxybenzaldehyde (*p*-anisaldehyde, PAA) from the photocatalytic selective oxidation of 4-methoxybenzyl alcohol, in aqueous (organic-free) TiO_2 suspensions, under mild conditions.

PAA is a compound used in sweet blossom and flavour compositions for confectioneries and beverages. It is an intermediate in many different industrial processes. For example, its hydrogen sulphite derivative is used as a brightener for metals in galvanic baths and it is employed in the synthesis of pharmaceuticals (especially antihistamines), agrochemicals, dyes and plastic additives.[11] PAA is present in many essential oils, usually together with anethole. It can be either a slightly yellowish or an uncoloured liquid with a sweet, mimosa, hawthorn odour and it is slowly oxidised to 4-methoxybenzoic acid (anisic acid) when exposed to air.

Industrial synthetic routes to PAA usually involve the oxidation of *p*-cresyl methyl ether in the presence of manganese dioxide and sulphuric acid. Recently, Reddy et al.[12] performed the selective oxidation of 4-methylanisole to PAA and anisic acid by using a $V_2O_5/Al_2O_3\text{-}TiO_2$ catalyst with a selectivity to PAA of 26%.

Results and Discussion

In the present study different samples of nanostructured TiO_2 catalyst were home prepared and used under near-UV radiation for oxidising 4-methoxybenzyl alcohol dissolved in water. The photocatalysts have been prepared by hydrolysis of $TiCl_4$ in deionised water at room temperature.[13] At the end of the controlled hydrolysis, the clear solution was boiled for different intervals of time (from 0.5 to 8 h) in order to obtain the final suspensions. Hereafter, the home prepared TiO_2 samples are indicated as HPx, x being the duration (in hour) of the boiling treatment. With this preparation method, filtration and calcination operations are not needed in order to obtain highly photoactive samples of nanostructured TiO_2 particles. The samples were characterised by means of X-ray diffractometry (XRD), determination of BET specific surface area (SSA) and primary particle size (by using Scherrer's equation) as well as scanning electron microscopic (SEM) observations.

Two different commercial catalysts, TiO_2 Merck (100% anatase) and TiO_2 Degussa P25 (*ca.* 20% rutile and *ca.* 80% anatase), were also tested for a comparison of their photoactivity with those of home-prepared TiO_2 samples.

XRD patterns of HP0.5 (Figure 1a) reveal that only the anatase phase is present, peaks at $2\theta = 25.5°$, 38.0°, 48.0°, 54.5°, all being assignable to anatase.

An increase of the boiling time to 2 h determines a better crystallinity of HP2 with only anatase as phase (Figure 1b). After 4 h boiling, HP4 shows a partial phase transformation of anatase to rutile (Figure 1c): peaks at $2\theta = 27.5°$, 36.5°, 56.5° (all assignable to rutile) are present. In Figure 1d, relative to HP6, the XRD peaks indicate that the presence of rutile is more significant than in the previous photocatalyst. The HP8 sample, obtained by increasing the boiling time up to 8 h, is almost pure rutile (Figure 1e). The peak at $2\theta = 25.5°$ (due to the anatase phase) disappears, while that at 36.5° is more intense than in the other diffractograms; moreover the peak at 56.5° is clearly visible.

The BET SSA values, reported in Table 1, are similar (*ca.* $220\,m^2\,g^{-1}$) for catalysts obtained by boiling the precursor for times from 0.5 up to 6 h. The least crystalline sample (TiO_2 HP0.5) shows the highest SSA, indicating that the increase of crystallinity favours the decrease of the SSA. For all these samples, the anatase phase was always present, although HP6 contained similar amounts of anatase and rutile. Conversely, HP8 (almost pure rutile) had a SSA value much lower than that of the other catalysts ($108\,m^2\,g^{-1}$) probably because agglomeration of particles occurred during catalyst preparation due to the prolonged boiling time. The primary particle sizes determined by means of Scherrer's equation of the home-prepared catalysts were in the 5–9 nm range, showing an increase with boiling time.

Figure 2 and Figure 3 are representative of our SEM observations of the various catalysts, carried out to determine particle dimensions: all the home-prepared samples were shown to be nanostructured, the average diameter of the smallest particles agglomerations being *ca.* 25 nm and we did not notice any significant differences among the various home-prepared TiO_2 samples.

The photoreactivity runs were carried out in a batch reactor with immersed lamp at atmospheric pressure and room temperature. The starting alcohol concentration was *ca.* 1.1 mM. The process performance was followed by measuring the values of alcohol and products concentration and calculating the substrate conversion and the aldehyde yield, i.e., the ratio between the produced moles of aldehyde and the moles of reacted alcohol. TOC (total organic carbon) was also measured for evaluating the percentage of mineralisation.

PAA was the main product obtained, CO_2 being the sole by-product. Under the used experimental conditions both alcohol and aldehyde are soluble in water (solubility values at 293 K are 14.5 mM and 31.5 mM, respectively) so that the homogeneity of the liquid

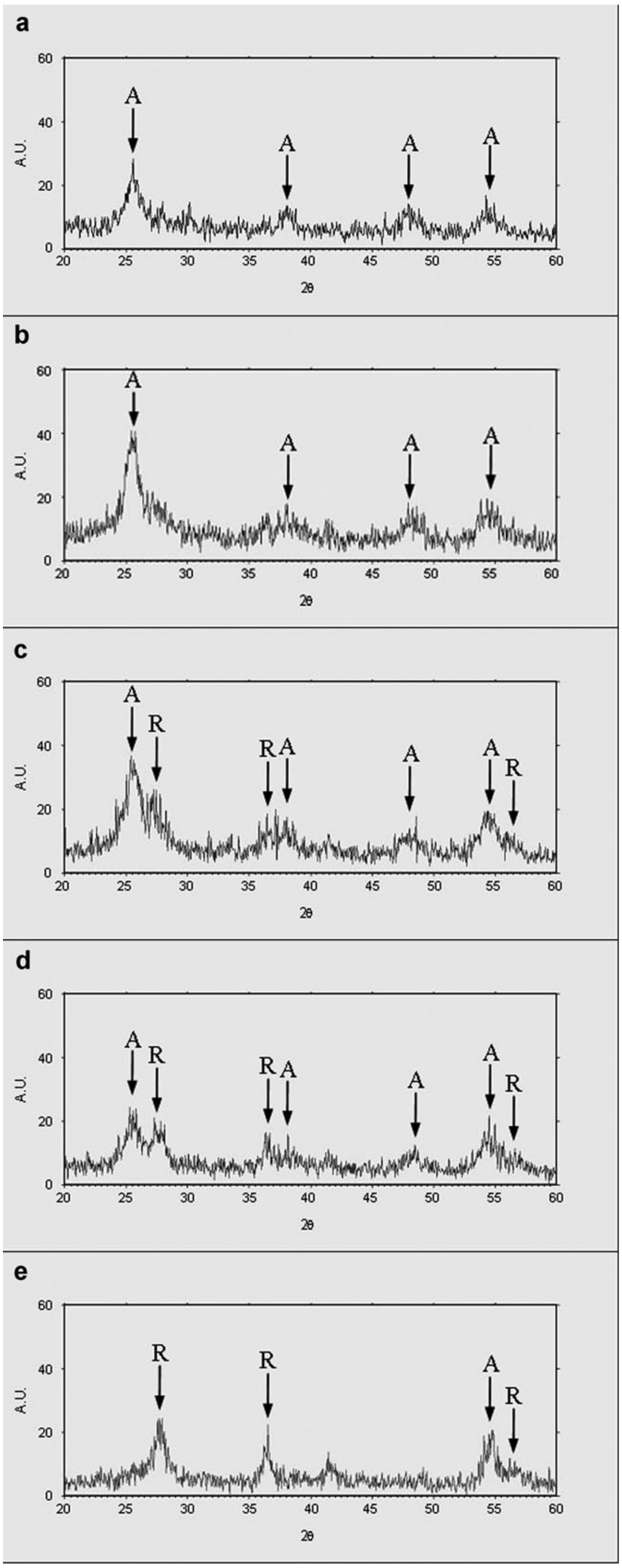

Figure 1. XRD patterns of home-prepared TiO_2 obtained from the same precursor boiled for various times. A: anatase; R: rutile. (**a**) HP0.5; (**b**) HP2; (**c**) HP4; (**d**) HP6; (**e**) HP8.

phase was always guaranteed. Sunlight was also used for irradiating the suspension; a few experimental runs were successfully carried out under these conditions achieving conversions and yields similar to those found by using artificial light even at far higher irradiation times.

Homogeneous runs were carried out in the absence of catalyst; after irradiating the alcohol solution for 6.5 h, a very low alcohol conversion (only 18.9%) was measured with an overall yield in aldehyde of 42.1% mol while the instantaneous yield continuously decreased with irradiation time. A typical run under homogeneous conditions is reported in Figure 4. It was also verified that in the presence of catalyst no reactions took place in the dark.

Preliminary experiments at different initial pH values (3, 7 and 11) were carried out by using TiO_2 Merck in an amount of $0.4\,g\,L^{-1}$. The pH was adjusted by using 0.1 M H_2SO_4 or 0.1 M NaOH aqueous solutions. All the molar yield values in aldehyde were calculated for conversions of 65% and were 9.5%, 11.7% and 9.0% at pH values of 3, 7 and 11, respectively (see Table 1). The reaction times needed to reach the above conversion were 3.9 h, 3.7 h, 4.2 h under acidic, neutral and basic conditions, respectively. On the basis of these results the neutral pH was chosen as the initial one for all the subsequent runs, and the suspension pH was adjusted in the case of home-prepared photocatalysts by using 0.1 M NaOH solution. The hourly conversion with the heterogeneous system was about 17.6% while the contribution of the homogeneous photoreaction to alcohol disappearance is about 2.9% under the best irradiation conditions, i.e., the conversion with catalyst is about 6 times higher than that achieved by homogeneous photooxidation. It may, therefore, be assumed that the homogeneous photooxidation rate is much lower than the heterogeneous one so that it may be neglected in analysing the reactivity results obtained in the presence of the catalyst.

At the end of each run both for the home-prepared and commercial catalysts the carbon balance was checked by taking into account the unreacted 4-methoxybenzyl alcohol, the produced PAA and CO_2. This balance was verified for a minimum of 97% mol when conversion was *ca.* 65%. The residual 3% may be attributed to modest quantities (not quantifiable) of open-ring products, supposed to be present since the HPLC chromatograms exhibited some small peaks having very low retention times. Traces of 4-methoxybenzoic acid were detected only for very long irradiation times (when conversion was higher than 80%). It is important to report that even for long lasting runs the catalyst powder did not show any modification and activity loss in the course of experiments.

In Figure 5 and Figure 6 the experiments that afforded the highest yields by using the two commercial

Table 1. Catalyst phase (A = anatase, R = rutile) and amount, BET specific surface area (SSA), initial pH of the suspension, irradiation time (for conversions of *ca.* 65%), yield in *p*-anisaldehyde, initial rate of alcohol disappearance, quantum efficiency (moles of produced PAA over moles of incident photons ×100).

TiO_2 Photocatalyst	SSA [$m^2 g^{-1}$]	Catalyst amount [$g L^{-1}$]	Initial pH	$t_{irrad.}$ [h]	Yield [% mol]	r_0 10^{12} [$mol s^{-1} m^{-2}$]	Φ [%]
Merck (A)	10	0.02	7	13.8	13.6	122	0.021
Merck (A)	10	0.1	7	6.5	12.3	48.7	0.038
Merck (A)	10	0.2	7	5.2	12.0	30.8	0.049
Merck (A)	10	0.4	3	3.9	9.5	19.7	0.050
Merck (A)	10	0.4	7	3.7	11.7	23.3	0.066
Merck (A)	10	0.4	11	4.2	9.0	14.7	0.043
Merck (A)	10	0.8	7	3.0	10.2	25.5	0.069
Merck (A)	10	2	7	1.8	10.0	32.2	0.110
P25 (A,R)	50	0.02	7	5.6	10.8	53.0	0.039
P25 (A,R)	50	0.1	7	1.9	10.0	164	0.108
P25 (A,R)	50	0.2	7	0.9	8.7	257	0.280
HP0.5 (A)	235	0.02	7	15.5	30.4	7.78	0.026
HP0.5 (A)	235	0.1	7	9.6	38.5	3.04	0.091
HP0.5 (A)	235	0.2	7	7.7	41.5	1.75	0.116
HP0.5 (A)	235	0.3	7	6.0	31.9	1.42	0.108
HP2 (A)	226	0.2	7	4.7	36.7	1.75	0.163
HP4 (A,R)	220	0.2	7	3.9	35.6	2.61	0.193
HP6 (A,R)	206	0.2	7	2.8	31.1	4.03	0.234
HP8 (R,A)	108	0.2	7	3.2	32.5	4.11	0.196

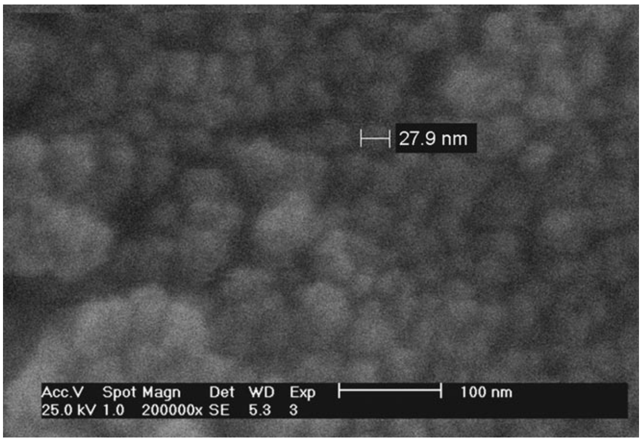

Figure 2. SEM image (magnification: ×200000) of HP0.5.

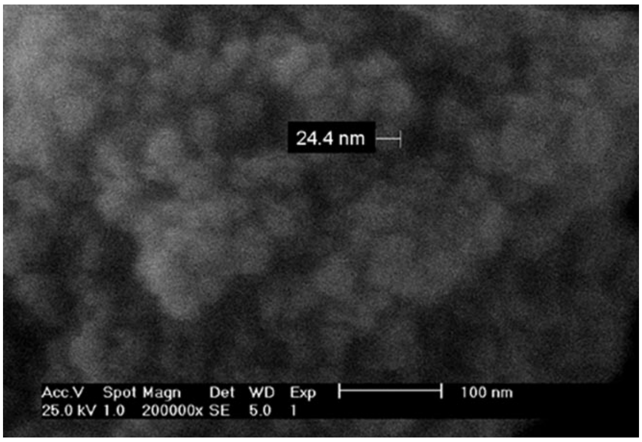

Figure 3. SEM image (magnification: ×200000) of HP8.

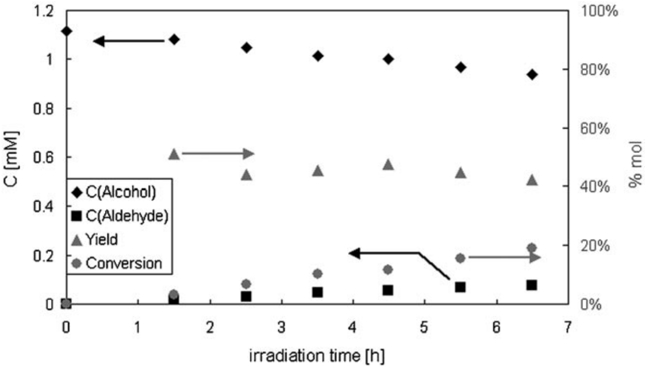

Figure 4. Experimental results of a homogeneous photooxidation representative run. 4-Methoxybenzyl alcohol conversion and PAA molar yield are shown.

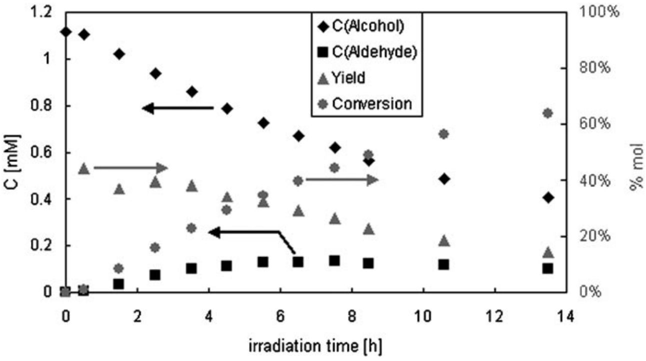

Figure 5. Experimental results of a photocatalytic oxidation representative run. 4-Methoxybenzyl alcohol conversion and PAA molar yield are shown. Catalyst: TiO_2 Merck (amount: 0.02 $g L^{-1}$).

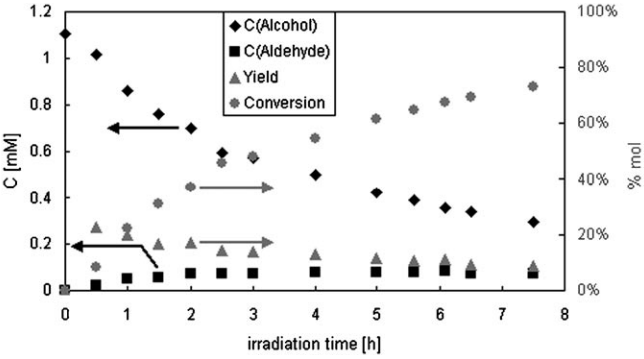

Figure 6. Experimental results of a photocatalytic oxidation representative run. 4-Methoxybenzyl alcohol conversion and PAA molar yield are shown. Catalyst: TiO_2 Degussa P25 (amount: 0.02 $g L^{-1}$).

photocatalysts (Merck and Degussa P25) are reported: the values of 4-methoxybenzyl alcohol and PAA concentrations together with the yield and conversion values *versus* irradiation time can be observed. Figure 7 reports the same values for the best home-prepared catalyst.

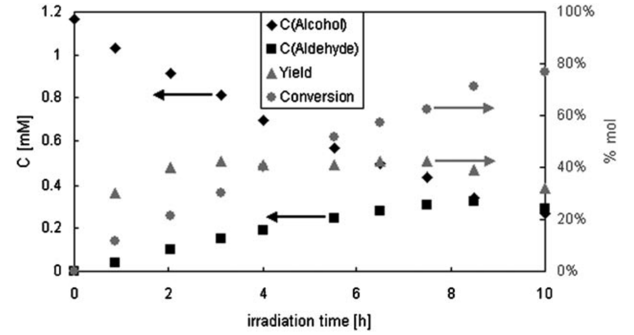

Figure 7. Experimental results of a photocatalytic oxidation representative run. 4-Methoxybenzyl alcohol conversion and PAA molar yield are shown. Catalyst: HP0.5 (amount: 0.2 $g L^{-1}$).

As far as the commercial catalysts are concerned, it can be observed that the yields values continuously decrease with irradiation time. Conversely, in Figure 7, it can be noticed that both the product concentration and the yield values increase, reach a maximum and start to decrease due to the oxidation of aldehyde to acid and formation of open-ring products and carbon dioxide. Nevertheless even at conversion values of 77%, the yield has an appreciable value of *ca.* 32%. These figures could be due to a remarkably lower photooxidation rate of the aldehyde with respect to alcohol in the presence of TiO_2.

Table 1 summarizes the most representative results of the photoreactivity runs performed by using home prepared and commercial catalysts. Various amounts of TiO_2 Merck and Degussa P25 were tested in the 0.02–2 $g L^{-1}$ range and the PAA yields increased on decreasing the catalyst amount. The best yield obtained with TiO_2 Merck was 13.6% with a catalyst amount of 0.02 $g L^{-1}$. The reaction time was 13.8 h. The best yield for TiO_2 Degussa P25 was 10.8% with a catalyst amount of 0.02 $g L^{-1}$. The reaction time was 5.6 h.

As far as the home-prepared catalysts are concerned, the HP0.5 was used with amounts in the 0.02–0.3 $g L^{-1}$ range. The best yield was obtained with 0.2 $g L^{-1}$ and it was equal to 41.5% mol with a reaction time of 7.7 h. This implies an improvement of about 3-fold in yield and 2-fold in reaction time compared with the best results achieved with Merck and an improvement of about 4-fold in yield with similar reaction times (7.7 h *versus* 5.6 h) with respect to Degussa P25.

It can be noticed that for TiO_2 P25 with a content of 0.2 $g L^{-1}$ the time needed to achieve conversions of 65% is shorter, but the corresponding yield (8.7%) indicates that most of the substrate has been transformed into other more oxidised products. For TiO_2 Merck this time is more similar to that determined for the home-prepared TiO_2 samples, but the yield in PAA is only 12.0%.

From the data reported in Table 1 it can be noticed that for the home-prepared catalysts the yield and the irradiation time needed to reach a conversion of 65% decreased by increasing the boiling time from 0.5 to 6 h, that is, the photooxidation process was faster towards both alcohol and aldehyde. These findings suggest that higher durations of the boiling treatment of the catalyst enhance its oxidising power, which is probably related to the sample crystallinity. In the case of HP6 the yield (31.1%) and the irradiation time (2.8 h) reach the lowest values. Among the home-prepared photocatalysts HP6 appears to be the most oxidising one. For HP8 both the yield (32.5%) and the irradiation time (3.2 h) slightly increase with respect to HP6.

The initial rates of the substrate oxidation and the estimated quantum efficiencies were also reported (see Table 1). It can be noticed that the highest rates were those of commercial catalysts, showing once again that a higher activity corresponds to a lower selectivity for partial oxidation. Remarkably, the quantum efficiency of home-prepared catalysts was instead comparable with that of Degussa P25 and higher than the Merck ones. This has significance as far as an efficient absorption of light is concerned. It should, however, be stressed that the light source was not optimised, hence higher values could be surely obtained.

It is worth noting that the most oxidising catalyst, among the home-prepared ones, showed the lowest yield value, and presented both the allotropic phases in similar amounts (see Figure 1d). Conversely the less oxidising catalyst, HP0.5, was the best one for the selective oxidation of 4-methoxybenzyl alcohol (see Table 1) and the least crystalline among the obtained catalysts. Remarkably, both commercial samples showed to be much more crystalline than all the home-prepared ones (diffractograms not shown for the sake of brevity).

Although a straightforward correlation of the photoactivity results with the bulk and surface physicochemical properties is not always easy, it can be highlighted that the experimental results reported in this paper indicate that the less crystallized TiO_2 samples (both as anatase and rutile phases) are significantly more selective towards the formation of PAA with respect to the commercial ones and yields in PAA up to 41.5% (with conversions of 65%) were achieved.

Conclusions

The selective oxidation of *p*-methoxybenzyl alcohol was performed in organic-free aqueous TiO_2 suspensions, obtaining a considerable yield of 41.5% mol. The synthesised catalysts, obtained under mild conditions, showed to be much more selective than two common commercial ones. In particular, TiO_2 Degussa P25, which is one of the best photocatalysts generally used for degradation purposes, showed a maximum yield of only 10.8% mol.

The initial alcohol concentration used in this work (*ca.* 1.1 mM) is quite low in comparison with that used for typical organic syntheses. For the practically development of photocatalytic syntheses it is necessary to have information on the scale-up of apparatus, that is, the volume of suspension and the time needed for obtaining a sensible amount of the target product. Owing to the highly non-linear phenomena occurring inside an irradiated suspension, the extrapolation of data would need a specific investigation. Work is in progress on these points.

The home-prepared catalysts' behaviour could be due to their low crystallinity compared with that of commercial ones, that are much more oxidising. In order to understand the reasons for the different photoactivity exhibited by the catalysts, detailed studies on their structural and surface properties must be carried out.

Experimental Section

The precursor solution was obtained by slowly adding 5 mL of $TiCl_4$ drop by drop into a 200-mL beaker containing 50 mL of water; during the addition, that lasted 5 min, the solution was magnetically stirred by a cylindrical bar (length, 3 cm; diameter, 0.5 cm) at 600 rpm. After that the beaker was closed and mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. This solution was transferred to a round-bottom flask having on its top a Graham condenser. The flask was put in boiling water, thus determining the boiling of the solution; the durations of the boiling were: 0.5, 2, 4, 6 and 8 h, obtaining a white suspension at the end of each treatment. The suspension was then dried at 323 K by means of a rotovapor machine (model Büchi Rotovapor M) working at 150 rpm, in order to obtain the final powdered catalysts.

The commercial and home-prepared catalysts were used in aqueous suspensions in a 0.5-L cylindrical batch photoreactor axially irradiated by a medium-pressure Hg lamp, continuously bubbling O_2. The dark equilibrium was reached before switching on the lamp after 30 min mixing. Average irradiance impinging onto the suspension was 10 $mW\,cm^{-2}$ (measured by using a radiometer UVX Digital, at $\lambda = 360$ nm).

The quantitative determination and identification of the species present in the reacting suspension was performed by means of a Beckman Coulter HPLC (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Luna 5µ Phenyl-Hexyl column (250 mm long × 2 mm i.d.), using Sigma–Aldrich standards. The retention times and UV spectra of the compounds were compared with those of an authentic sample. The eluent consisted of: 17.5% acetonitrile, 17.5% methanol, 65% 40 mM KH_2PO_4 aqueous solution. Retention times were 8.7 min for 4-methoxybenzyl alcohol and 17.2 min for *p*-anisaldehyde and areas were calculated at $\lambda = 225$ nm.

TOC analyses were carried out by using a 5000 A Shimadzu TOC analyser. XRD patterns of the powders were recorded by a Philips diffractometer using the Cu Kα radiation and a 2θ scan rate of 1.2°/min. SEM images were obtained using a model Philips XL30 ESEM microscope, operating at 25 kV on samples sprayed on the stab and dried at room temperature, upon which a thin layer of gold had been evaporated. BET specific surface areas were measured by the multi-point BET method using a Nova Quantachrome 2000E.

All the used chemicals were purchased from Sigma–Aldrich with a purity > 99.0%.

Further information about the experimental set-up (concerning the used reactor and lamp) and product identification can be found in the Supporting Information.

Acknowledgements

The authors wish to thank Drs. M. Addamo and M. Bellardita for the great help given in the catalyst preparation. The financial support from MIUR (Rome) is gratefully acknowledged.

References

[1] G. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639.

[2] R. A. Sheldon, I. W. C. E. Arends, G. ten Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781.

[3] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362–365.

[4] C. Li, L. Chen, *Chem. Soc. Rev.* **2006**, *35*, 68–82.

[5] K. Ohkubo, K. Suga, S. Fukuzumi, *Chem. Commun.* **2006**, *19*, 2018–2020.

[6] M. A. Gonzalez, S. G. Howell, S. K. Sikdar, *J. Catal.* **1999**, *183*, 159–162.

[7] T. Caronna, C. Gambarotti, L. Palmisano, C. Punta, F. Recupero, *Chem. Commun.* **2003**, 2350–2351.

[8] U. R. Pillai, E. Sahle-Demessie, *J. Catal.* **2002**, *211*, 434–444.

[9] O. S. Mohamed, A. E. M. Gaber, A. A. Abdel-Wahab, *J. Photochem. Photobiol., A* **2002**, *148*, 205–210.

[10] S. Farhadi, M. Afshari, M. Maleki, Z. Badazadeh, *Tetrahedron Lett.* **2005**, *46*, 8483–8486.

[11] *Flavors and Fragrances*, in: *Ullmann's Encyclopedia of Industrial Chemistry*, (Release 2006, 7th edn.), Wiley-VCH, Weinheim, and references cited therein.

[12] B. M. Reddy, K. N. Rao, G. K. Reddy, P. Bharali, *J. Mol. Catal. A: Chem.* **2006**, *253*, 44–51.

[13] M. Addamo, V. Augugliaro, A. Di Paola, E. García-López, V. Loddo, G. Marcì, R. Molinari, L. Palmisano, M. Schiavello, *J. Phys. Chem. B* **2004**, *108*, 3303–3310.