# Nanostructured Rutile TiO₂ for Selective Photocatalytic Oxidation of Aromatic Alcohols to Aldehydes in Water

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Since the 1970s heterogeneous photocatalysis has been successfully applied to degrade harmful molecules on the basis of the generally accepted statement that this method is quite unselective especially for oxidation performed in water. The degradation processes are generally carried out using commercial specimens of anatase or anatase/rutile mixed phases (such as Degussa P25). Recent results have however highlighted that photocatalysis[1] may also play a role in the field of organic syntheses as it is able to perform various reactions among which the partial oxidation of −CH₂OH group to −CHO is one. This is a key reaction for the production of many organic products, since aldehyde derivatives are widely used in the flavor, confectionary, and beverage industries.[2]

The selective oxidation of 4-methoxybenzyl alcohol[3] to the corresponding aldehyde (*p*-anisaldehyde) has been carried out in aqueous TiO₂ suspensions in mild conditions with high yields. It was found[3] that home-prepared anatase TiO₂ samples are more selective than commercial ones (Degussa P25 or Merck TiO₂).

Rutile TiO₂ catalyst shows generally less photoactivity than anatase; it is commonly prepared by calcination of anatase TiO₂ at high temperature.[4] Some authors however report preparations of rutile at low-temperature giving rise to a catalyst with an appreciable photoactivity.[5] In this work home-prepared samples of rutile TiO₂ have been used in performing the partial oxidation of benzyl alcohol (BA) and *p*-methoxybenzyl alcohol (MBA) to the corresponding aldehydes (benzaldehyde, BAD, and 4-methoxybenzaldehyde, PAA) in water free of any organic cosolvent. The selectivity values obtained by these samples are the highest ones ever reported for TiO₂ photocatalysts.

The rutile preparation exploits a new sol−gel route ex TiCl₄. A white sol made by hydrolyzing TiCl₄ in water was kept closed in an oven for 2 days at 333 K. Then the suspension was dried at 333 K by means of a rotovapor machine to obtain the final powdered catalyst which is hereafter indicated as HP333.

To check the influence of the degree of crystallinity on the photoreactivity, HP333 was calcined at 673 or 973 K. The obtained samples were coded HP673 and HP973, respectively.

An amorphous TiO₂ catalyst (HP298) was also prepared by a TiCl₄/water (1/11 v/v) sol, magnetically stirred for 10 h, to obtain a clear solution. Subsequently 1 M NaOH solution was added to neutralize the HCl formed.

XRD spectra of the prepared samples and of commercial rutile (Sigma-Aldrich, SA) are shown in Figure 1. The peaks assignable to rutile are those at $2\theta = 27.5°, 36.5°, 41°, 54.1°,$ and $56.5°$. The crystallinity increases with treatment temperature. In particular the catalyst prepared at room temperature is completely amorphous (no peak, even broad, is present), whereas HP333 shows some
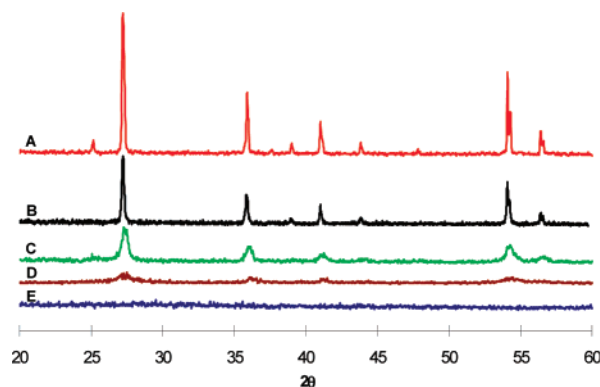
**Figure 1.** XRD patterns of home-prepared and commercial TiO₂: (A) SA; (B) HP973; (C) HP673; (D) HP333; (E) HP298.

crystallinity, but less than HP673, HP973, and SA. The last sample, that is, the most crystalline, shows also a very minor presence of anatase phase (see peak at $2\theta = 25.5°$ in Figure 1). Table 1 shows how crystallite size (calculated from the Scherrer's equation) increases with treatment temperature along with the degree of crystallinity. BET surface area of crystalline samples, conversely, follows an opposite trend (ranging from 4 to 107 m²/g, see Table 1). This phenomenon is clearly due to particles growth and sintering effects occurring at high temperatures, yielding a decrease in surface area. Moreover SEM images (shown in Supporting Information, Figure S1) highlight that the dimensions of crystallite primary agglomerates range from ca. 50 to 240 nm, increasing with crystallinity of samples. A cylindrical Pyrex batch photoreactor (volume: 0.5 L) with an immersed lamp (125W, Hg medium pressure) was used to perform the reactivity experiments.

The process performance was followed by measuring the values of alcohol and product concentration and calculating the substrate conversion and the selectivity toward aldehyde. Total organic carbon (TOC) was also measured for evaluating the percentage of mineralization, that is, the amount of CO₂. No reaction occurred in the dark, even in the presence of catalyst and bubbling oxygen, as expected.

Irradiating the alcohol solutions in the absence of catalyst gave rise to reactivity, from 10 to 50 times slower than the heterogeneous systems, so the homogeneous contribution will be neglected in the further discussion.

The highest selectivity in the photocatalytic oxidation of both alcohols was found with HP333. In particular, BA oxidation gave the maximum selectivity with a HP333 catalyst amount of 0.4 g/L (Table 1). To compare the selectivity of this sample with the others we used 0.4 g/L catalyst for all the runs, although surface areas of samples change very much. Even by significantly varying the amount of SA, selectivity was always far lower than that of HP333.

***Table 1.*** BET Specific Surface Area, Crystallite Size of Catalysts and Their Photocatalytic Performance[a]

| catalyst | SSA [m²/g] | crystallite size [nm] | catalyst amount [g/L] | $t_{irr}$ [h][b] | selectivity [% mol][b] |
|---|---|---|---|---|---|
| homogeneous | | | | 176 | 14.0 |
| HP298 | 215 | | 0.4 | 22 | 12.0 |
| HP333 | 107 | 7 | 0.2 | 17 | 38.0 |
| HP333 | 107 | 7 | 0.4 | 8.4 | 38.2 |
| HP333 | 107 | 7 | 0.6 | 8.95 | 37.7 |
| HP333-MBA | 107 | 7 | 0.4 | 2.36 | 60.0 |
| HP673 | 35 | 13 | 0.4 | 6 | 12.0 |
| HP973 | 4 | 41 | 0.4 | 9.4 | 9.9 |
| SA | 2.5 | 52 | 0.4 | 3.75 | 9.2 |
| SA-MBA | 2.5 | 52 | 0.4 | 2.15 | 20.9 |

[a] The experimental results refer to BA oxidation, except that indicated as HP333-MBA and SA-MBA, referring to MBA oxidation. [b] Irradiation time ($t_{irr}$) and selectivity (to aldehyde) are calculated for an alcohol conversion of 50%.
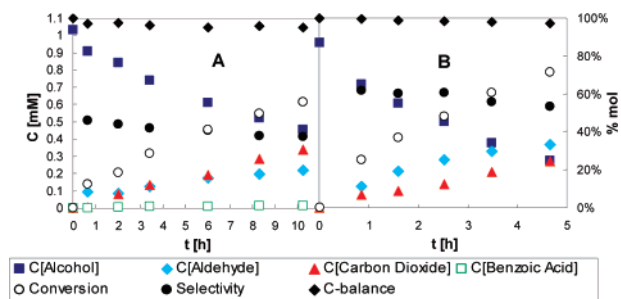


***Figure 2.*** Experimental results of a representative oxidation run of (A) BA and (B) MBA with HP333 (amount: 0.4 g/L). Conversion, selectivity, and C-balance are scaled on right side. The $CO_2$ concentration values were divided by 7 (A) or 8 (B) for normalization purposes.

Figure 2 shows the results of representative experimental runs carried out by oxidizing the two alcohols with HP333. Two parallel reaction routes are present from the start of irradiation: partial oxidation to aldehydes and mineralization to $CO_2$:[3]

$$CO_2 \leftarrow ArCH_2OH \rightarrow ArCHO$$
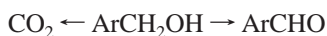
The disappearance of substrates along with the production of aldehydes, $CO_2$, and traces of acid (only for BA oxidation) can be observed. Conversion and selectivity to aldehyde are also reported, as a function of irradiation time. During MBA and BA oxidation, the selectivity slowly decreases during the reaction because of overoxidation, but maintains the values of ca. 38 and 60% mol, respectively, even when the conversion reaches 50%. These values are surprisingly high if we consider that the reaction takes place in water with a $TiO_2$-mediated photocatalytic process. The selectivity to aldehyde in MBA oxidation is higher than that in BA; it can be explained by considering the presence (in MBA) of the electron-releasing methoxy group in the para position.[6]

Carbon balances of each run, carried out with HP333, were verified by taking into account the unreacted alcohol, the produced aldehyde, the amounts of acid and $CO_2$. The carbon balance was quantified as ca. 96% and 98%, for BA and MBA, respectively, when conversion was 50%. The small loss may be ascribed to the production of open-ring aromatic compounds coming from over-oxidation of aldehyde and acid.

The catalyst affects alcohol oxidation in a crucial way; a selectivity variation ranging from ca. 9 to 38% in the case of BA oxidation and from ca. 21 to 60% in that of MBA was observed. The photoreactivity results reported in Table 1 allow comparison of the performance of some home-prepared rutile samples with a commercial one. It is worth noting that selectivity increases by decreasing the crystallinity of samples (Figure 1) but the reaction rate appears similar, except for SA, which was the most oxidizing catalyst tested. The best performing catalyst was the badly crystallized HP333 that gave a selectivity of ca. 38 and 60% mol for BA and MBA, respectively. It should be noted that the oxidation of MBA by home-prepared anatase prepared by following a different procedure reported previously[3] gave a value of only 41%.

To study the influence of crystallinity, the calcined samples HP673 and HP973, along with an amorphous $TiO_2$ (HP298), were tested. The last catalyst gave rise to a very low reaction rate and selectivity (ca. 12% mol) probably because the oxidation power is so low that the reaction mechanism and the physicochemical nature of sites deeply change with respect to HP333. HP673 gave a selectivity drastically lower than HP333 (12 vs 38% for BA), but the time needed for conversion was lower than that of HP333 (see Table 1). On the contrary, by calcining at 973 K, both selectivity and reaction rate decrease, and the latter phenomenon could be due to a decrease of the surface hydroxyl groups, caused by the high temperature. The most crystalline catalysts gave rise to many highly oxidized intermediates (in HPLC chromatograms peaks with low retention times were present) that result in a significant drop in selectivity.

Finally the obtained results suggest that selectivity is not affected in a considerable way by the reaction-rate value. On the contrary adsorption can play a role; in fact it was found that the extent of PAA adsorption on HP333 is negligible with respect to that of BAD (23%). Selectivity differences between the formation of BAD and PAA (38 vs 60%) can be justified by considering the very different adsorption extent of BAD and PAA. The hydrophobic character of BAD determines its strong adsorption over HP333 surface and by preventing its desorption gives rise to its further oxidation.

In conclusion, we have used for the first time a home-prepared rutile $TiO_2$ for selective oxidation of aromatic alcohols to aldehydes in water suspensions. The experiments point to a primary influence of crystallinity on selectivity. The highest selectivity was attained with the badly crystallized HP333.

**Supporting Information Available:** Experimental details; SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

(1) (a) Palmisano, G.; Augugliaro, V.; Pagliaro, M.; Palmisano, L. *Chem. Commun.* **2007**, 3425. (b) Kisch, H. *Adv. Photochem.* **2001**, *62*, 93. (c) Mills, A.; Le Hunte, S. *J. Photochem. Photobiol. A* **1997**, *108*, 1. (d) Maldotti, A.; Molinari, A.; Amadelli, R. *Chem. Rev.* **2002**, *102*, 3811. (e) Caronna, T.; Gambarotti, C.; Palmisano, L.; Punta, C.; Recupero, F. *Chem. Commun.* **2003**, 2350. (f) Ohtani, B.; Kawaguchi, J.; Kozawa, M.; Nakaoka, Y.; Nosaka, Y.; Nishimoto, S. *J. Photochem. Photobiol. A* **1995**, *90*, 75. (g) Hörner, G.; Johne, P.; Kunneth, R.; Twardzik, G.; Kisch, H. *Chem. Eur. J.* **1995**, *5*, 208. (h) Cemenati, C.; Richter, C.; Albini, A. *Chem. Commun.* **1998**, 805. (i) Marinkovic, S.; Hoffmann, N. *Eur. J. Org. Chem.* **2004**, 3102. (j) Palmisano, G.; Addamo, M.; Augugliaro, V.; Caronna, T.; García López, E.; Loddo, V.; Palmisano, L. *Chem. Commun.* **2006**, 1012.

(2) (a) Mao, Y.; Bakac, A. *Inorg. Chem.* **1996**, *35*, 3925. (b) Pillai, U. R.; Demessie, E. S. *J. Catal.* **2002**, *211*, 434. (c) Mohamed, O. S.; Gaber, A. E. M.; Abdel-Wahab, A. A. *J. Photochem. Photobiol. A* **2002**, *148*, 205. (d) Green, K. J.; Rudham, R. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1867.

(3) Palmisano, G.; Yurdakal, S.; Augugliaro, V.; Loddo, V.; Palmisano, L. *Adv. Synth. Catal.* **2007**, *349*, 964.

(4) Addamo, M.; Augugliaro, V.; Di Paola, A.; García López, E.; Loddo, V.; Marcì, G.; Molinari, R.; Palmisano, L.; Schiavello, M. *J. Phys. Chem. B* **2004**, *108*, 3303.

(5) (a) Nag, M.; Basak, P.; Manorama, S. V. *Mater. Res. Bull.* **2007**, *42*, 1691. (b) Yin, S.; Li, R.; He, Q.; Sato, T. *Mater. Chem. Phys.* **2002**, *75*, 76. (c) Li, L.; Liu, J.; Jia, Z. *Mater. Lett.* **2006**, *60*, 1753.

(6) Jenzer, G.; Sueur, D.; Mallat, T.; Baiker, A. *Chem. Commun.* **2000**, 2247.

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