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Oxidation of Aromatic Alcohols in Irradiated Aqueous Suspensions of Commercial and Home-Prepared Rutile TiO_2: A Selectivity Study

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Abstract: The photocatalytic oxidation of benzyl alcohol (BA) and 4-methoxybenzyl alcohol (MBA) has been performed in pure water by using commercial TiO_2 samples (Sigma-Aldrich, Merck, Degussa P25) and rutile TiO_2 prepared from $TiCl_4$ at low temperature. Particular attention has been devoted to the identification of the produced aromatic compounds along with the formed CO_2. Oxidation products such as the corresponding aromatic aldehyde and acid, as well as mono- and dihydroxylated aldehydes have been detected. The home-prepared rutile sample showed a marked selectivity towards the formation of the aromatic aldehyde (38 and 60 % for BA and MBA, respectively), resulting in a three- to sevenfold improvement relative to commercial samples, with the only byproduct being CO_2. This catalyst was found to be the most selective in the formation of aldehyde in water. By using the commercial or the calcined home-prepared samples, many hydroxylated aromatic compounds were detected besides the aldehyde and the acid. This finding points to a higher selectivity performance of the home-prepared rutile relative to the commercial TiO_2 samples. Some of the home-prepared samples were also dialysed to check the influence of the presence of Cl^- species on catalyst reactivity and selectivity. We have attempted to explain the different reaction rate and selectivity observed for MBA and BA.

Keywords: alcohols · oxidation · photocatalysis · rutile · selectivity

Introduction

Since the discovery of TiO_2 properties through irradiation,[1] which resulted in the chemical mediation of redox processes, heterogeneous photocatalysis has been mainly employed to degrade organic and inorganic pollutants in water or air; it has also been coupled with other technologies.[2] Rutile is the most stable among TiO_2 phases even in strongly acidic or basic conditions and it is applied in optical devices, energy resources, high-quality paints and cosmetics. For photocatalytic reactions, however, the most-used crystalline phase has been anatase or anatase–rutile mixtures, whereas pure rutile has been typically considered less (or even not) active. Nevertheless, many preparations of active rutile have been reported during the last two decades.[3] Preparation of rutile has been performed in most cases by calcining anatase or amorphous samples at approximately 1000 K, but even some rutile syntheses at low temperature have been reported with better results in terms of activity.[4]

Photocatalytic-selective reactions for synthetic purposes are not as common as degradations but have been carried out,[5] although they have been mainly performed either in organic solvents or in the gas phase.[6] However, hydrocarbon oxidation,[7] aromatic hydroxylation,[8] naphthalene oxygenation,[9] heterocycle functionalisation[10] and cyclisation of amino acids[11] are some of the few studies related to the selectivity of photocatalytic reactions in water.

The need to work on sustainable green chemical routes is today of primary importance, and photocatalysis, especially when carried out in organic-free solvents, offers a number of

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advantages, the most relevant of which is the use of the sun as a green and free energy source, even if one considers the small portion of the solar spectrum that falls into the UV region. Moreover, heterogeneous photocatalysis requires neither unhealthy, dangerous heavy-metal catalysts nor strong chemical oxidant/reducing species to carry out chemical processes at measurable rates.

Selective oxidation of hydroxyl groups can be considered a key step in many organic syntheses. Hence, one of the main goals of current chemistry has been to eliminate the environmentally harmful conditions in which this process has usually been carried out,[12] a process that generally involves organic solvents at high temperature and pressure as well as stoichiometric oxygen donors (such as chromate and permanganate) that are not only expensive and toxic, but also produce large amounts of dangerous waste.

Photocatalytic alcohol oxidation has been carried out either in acetonitrile[13] or in air,[14] but partial oxidation of aromatic alcohol has only recently been carried out in suspensions of water and home-prepared anatase TiO_2,[15] which was obtained by boiling a solution of $TiCl_4$. 4-Methoxybenzyl alcohol (MBA) was partially oxidised to 4-methoxybenzaldehyde with a selectivity of approximately 41% for an alcohol conversion of 65%. This paper reports a new method of TiO_2 preparation from aqueous solutions of $TiCl_4$ kept at low temperature (333 K) to yield a rutile phase, which allowed a selectivity of approximately 60% to be obtained under the same experimental conditions as those previously reported.[15] It also shows how the partial oxidation to aldehyde can be carried out with a good selectivity (ca. 38%) in the case of benzyl alcohol (BA). The obtained results have been compared with those of three commercial samples: Sigma-Aldrich (rutile), Degussa P25 (rutile 20%, anatase 80%) and Merck (anatase), each of which showed a much lower selectivity, even if used in optimised amounts. Both commercial and home-prepared samples were characterised by using XRD, BET specific surface area determination and SEM. Moreover, the TiO_2 home-prepared sample was dialysed or calcined (at 673 or 973 K) to investigate the effect of residual Cl^- ions and heating temperature on crystallinity, and hence reaction rate and selectivity.

The concentrations of aromatic alcohols and their oxidation products were monitored during irradiation, and the amount of mineralisation was recorded by means of a total organic carbon (TOC) analyser. The aromatic molecules obtained from the oxidation were identified by using HPLC and GC–MS analyses. The different BA and MBA reaction rates and selectivities towards aldehyde are discussed and an explanation is provided on the basis of our results.

Results and Discussion

Catalysts: In the present study the oxidation of BA and of MBA was performed in a batch photoreactor that contained aqueous suspensions of home-prepared rutile. Commercial samples, consisting of rutile (Sigma-Aldrich), anatase (Merck) or mixtures of the two phases (Degussa P25) were employed for comparative purposes.

The home-prepared samples were synthesised from solutions of $TiCl_4$. They were prepared by hydrolysing $TiCl_4$ at room temperature and by treating the resulting solids at different temperatures (up to 973 K) to attain the various samples. The catalysts are hereafter referred to as “HP” followed by a number, which indicates the treatment temperature in kelvin.

Figure 1 shows the XRD patterns of all of the catalysts. The pattern of HP298, which was prepared at room temperature, does not show any peaks to indicate crystallinity, probably due to the very small size of particles and to the substantial amorphousness of this sample. HP333, prepared by simply keeping the solution of $TiCl_4$ at 333 K for two days, is made of a badly crystallised rutile phase. Upon calcining HP333, crystallinity increased with the temperature treatment; the HP973 diffractogram seems quite similar to that of the Sigma-Aldrich rutile.

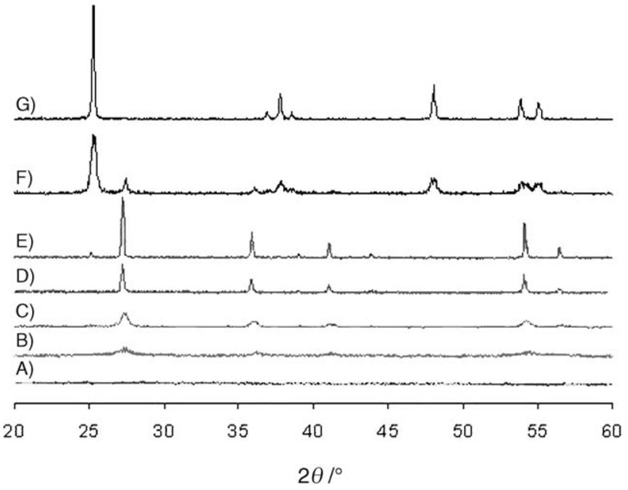


Figure 1. XRD patterns of home-prepared and commercial TiO_2: A) HP298; B) HP333; C) HP673; D) HP973; E) Sigma-Aldrich; F) Degussa P25; G) Merck.

Crystallite and particle agglomeration size along with specific surface area (SSA) strongly change with treatment temperature (see Table 1). Primary crystallite size, determined by using the Scherrer equation, shifts from 7 to 41 nm for home-prepared catalysts, whereas commercial samples show sizes ranging from 30 to 60 nm. The highest values were observed for HP973 and for commercial TiO_2, that is, the most crystalline catalysts. Particle agglomeration, measured by using SEM images (not shown for the sake of brevity), varies from approximately 50 to 215 nm, increasing with preparation temperature. Specific surface area, along with crystallite size, depends on the temperature used during the preparation process. These qualities drastically decrease and increase, respectively, by raising the temperature. SSA values between 4 and 215 $m^2 g^{-1}$ were obtained for home-

Table 1. Preparation temperature, BET specific surface area, and crystallite size of the catalysts and their photocatalytic performance for the oxidation of aromatic alcohols to aldehydes (catalyst amount: 0.4 $g L^{-1}$).

Catalyst	SSA $[m^2 g]$	Crystallite size [nm]	$t_{irr.}$[a] BA [h]	Selectivity[a] BA [% mol]	$t_{irr.}$[a] MBA [h]	Selectivity[a] MBA [% mol]
HP298	215	–	22.0	12.1	–	–
HP333	107	7	8.4	38.2	2.36	60.0
HP333D	107	7	5.3	33.5	2.18	56.2
HP673	35	13	6.0	12.2	2.20	50.1
HP973	4	41	9.4	9.9	3.81	40.0
Sigma-Aldrich	2.5	52	3.8	9.2	2.15	20.9
Merck	10	60	2.0	7.9	1.50	15.9
Degussa P25	50	30	1.0	7.8	0.72	8.3

[a] $t_{irr.}$ (irradiation time) and selectivity (to aldehyde) refer to an alcohol conversion of 50%. Selectivity = (formed aldehyde)/(converted alcohol).

prepared samples, with the lowest ones being very close to that of the Sigma-Aldrich sample.

Photoreactivity experiments: Preliminary runs indicated that no conversion of either alcohol was observed when the experiment was carried out in a dark environment, both in the absence and in the presence of catalyst, even when continuously bubbling oxygen through the sample. Moreover, oxidation of BA and MBA was carried out in irradiated aqueous solutions, but in the absence of a catalyst under experimental conditions similar to those used during the heterogeneous experiments. BA and MBA conversion of 50% required reaction times of 176 and 21 h, respectively. As this conversion was reached in much shorter times in photocatalytic runs, it may be assumed that the homogeneous oxidation process plays a negligible role in our heterogeneous systems.

Photocatalytic oxidation runs were carried out with amounts of HP333 in the range of 0.2 to 0.6 $g L^{-1}$ to determine the amount of catalyst capable of maximising the selectivity towards aldehyde (calculated as the ratio between the formed aldehyde and the converted alcohol). This study showed that the selectivities are indeed very close to each other, regardless of the amount of catalyst. Reaction rate values are quite different; they increase when using a catalyst amount from 0.2 to 0.4 $g L^{-1}$ and remain constant for higher amounts of catalyst, thus indicating that for those amounts all of the emitted photons are absorbed by the suspension. Consequently, the catalyst amount used in all of the BA and MBA oxidation runs was 0.4 $g L^{-1}$. Based on the above data, this quantity also determined the lowest irradiation time needed to reach 50% alcohol conversion. All of the other runs were performed with this amount of TiO_2 to compare the results obtained with HP333 with those of other catalysts. It should be emphasised that the irradiated surface of the samples used was very different in some cases. Selectivity, however, was not significantly influenced in any case by the amount of solid present in the reacting medium. The catalyst amounts were decreased to 0.02 $g L^{-1}$, thus highlighting that even in this case selectivity does not change considerably for all of the catalysts.

From the start of irradiation two parallel reaction pathways take place: direct mineralisation to CO_2 (occurring through a series of reactions occurring over the catalyst surface and producing intermediates not desorbing to the bulk of the solution) and partial oxidation to aldehyde. The importance of each of these pathways depends on the physicochemical and structural properties of the catalyst, and also on the features of the reacting alcohols and produced aldehydes.

During the BA and MBA photocatalytic oxidation, CO_2 was detected and the main products formed were determined by using TOC and HPLC analyses, respectively. Only when commercial or calcined (HP673 and HP973) catalysts were used did we detect CO_2 and the corresponding aromatic aldehydes together with many other products, such as mono- and dihydroxylated aldehydes. On the contrary, for HP333 the predominant products were the corresponding aldehydes and CO_2, the other products were present only as traces. During BA oxidation, traces of benzoic acid were also found no matter which catalyst was used.

Figures 2 and 3 show the trends of the reagent and main products (aldehyde and CO_2) during the photocatalytic oxidation of BA and MBA carried out with the Sigma-Aldrich

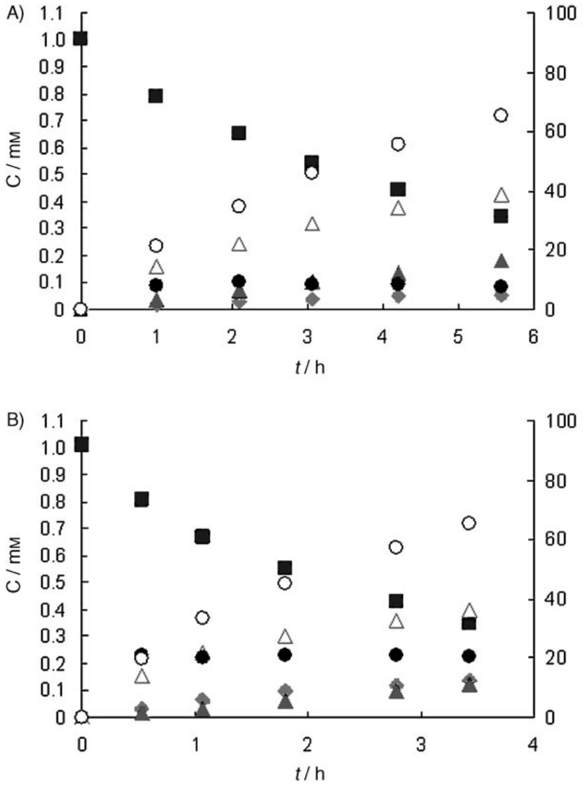


Figure 2. Experimental results of a representative oxidation run of BA (A) and MBA (B) with rutile TiO_2 from Sigma-Aldrich. Conversion (○) and selectivity (●) are scaled on the right side. The CO_2 (▲) concentration values were divided by 7 (A) or 8 (B) for normalisation purposes. ■: [alcohol], ◆: [aldehyde] and △: [other species].

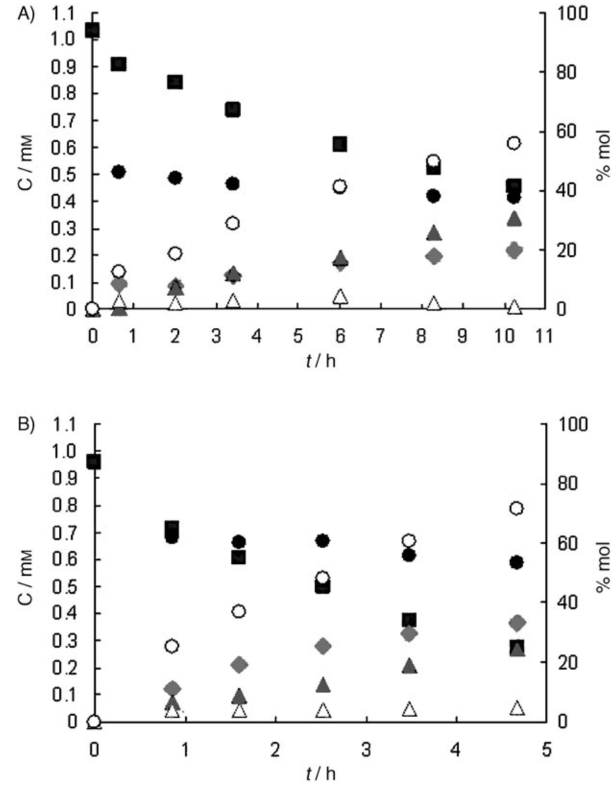


Figure 3. Experimental results of a representative oxidation run of BA (A) and MBA (B) with rutile TiO_2 HP333. Conversion (○) and selectivity (●) are scaled on the right side. The CO_2 (▲) concentration values were divided by 7 (A) or 8 (B) for normalisation purposes. ■: [alcohol], ◆: [aldehyde] and △: [other species].

rutile and with the best-performing home-prepared rutile (HP333).

The global amount of the organic carbon belonging to identified (but not quantified separately) and unidentified (mainly open-ring products) compounds is also reported. The values reported in Figures 2 and 3 were evaluated from the difference between initial TOC and the sum of residual alcohol, produced aldehyde and CO_2 (quantified from the extent of mineralisation, measured by TOC analysis). The figures also show conversion and selectivity values versus irradiation time. This highlights how selectivity slowly decreases during reaction time.

The commercial Sigma-Aldrich, Merck and Degussa P25 samples produced a significant number of species different from aldehyde and carbon dioxide (Figure 2), whereas HP333 did not support the production of other species (Figure 3). This different behaviour can be ascribed to the considerable presence of hydroxylated aromatic compounds and open-ring products, which were visible in HPLC chromatograms at very low retention times only when commercial and calcined samples were used.

The activity of the home-prepared rutile samples was always much lower than that of commercial catalysts. HP333 needed 8.4 h to reach 50 % BA conversion, against 3.8, 2.0 and 1.0 h for Sigma-Aldrich, Merck and Degussa P25 samples, respectively. Interestingly, an increase in crystallinity by means of thermal treatment resulted in selectivities even lower than that of HP333.

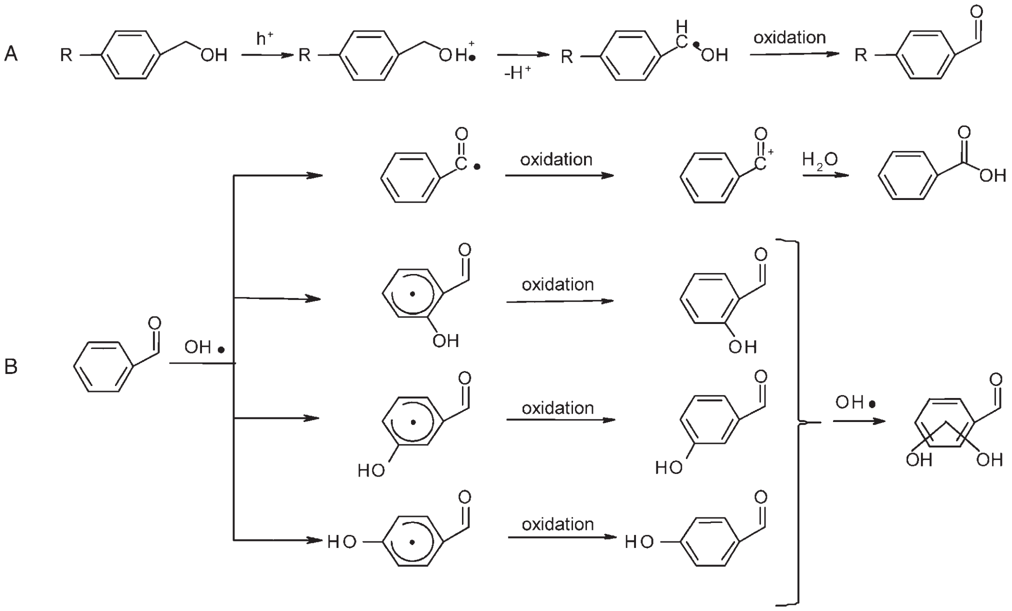
The most selective rutile sample was HP333 (Table 1), and the selectivity values drastically decreased from 38.2 to 9.9 % mol (for BA) by increasing the treatment temperature at which this catalyst was subjected. The selectivity of commercial TiO_2 catalysts was four to five times lower than that of HP333, of which the least selective sample was Degussa P25. As far as MBA is concerned, the selectivity decreased from 60 % mol for HP333 to 8.3 % mol for Degussa P25.

The reported selectivity clearly shows an opposing trend with respect to catalyst activity if comparing HP333 with commercial samples. The most active catalysts (commercials) are the least selective in the formation of aldehyde. Furthermore, by comparing home-prepared samples, one can understand how increasing the treatment temperature results in decreasing selectivity; this phenomenon can be ascribed to a drastic depletion of the surface hydroxylation of HP673 and HP973.

HP333 powder was subjected to a dialysis treatment to study the influence of chloride ions on selectivity, as the samples obtained from $TiCl_4$ can contain not negligible residuals of Cl^-. The results attained with HP333D (the dialysed sample) highlighted only a small decrease in selectivity (from 38.2 to 33.5 % for BA), whereas a significant increase in activity was evidenced: irradiation time needed to convert 50 % of the initial alcohol decreased from 8.4 to 5.3 h. This finding, which points to a higher mineralisation when using the dialysed sample, can be explained by the well-known detrimental effect of Cl^- ions owing to their good properties as hole traps.[16]

Finally, the run carried out with the catalyst synthesised at 298 K, by simply adding an aqueous solution of NaOH to a clear solution of $TiCl_4$, gave worse results than that using HP333 in terms of both activity and selectivity. The former can be attributed to the absence of crystallinity highlighted by XRD analysis (Figure 1). The reaction time needed to reach 50 % conversion was, however, 22 h, a much lower figure than that found during the homogeneous reaction (176 h). In any case, the catalyst was found to be active, and this insight could be explained by two different hypotheses: 1) the presence of small amounts of crystallites, not detectable through XRD analysis; 2) the occurrence of a photoreaction in the adsorbed phase. On the other hand, selectivity was considerably lower than that of HP333, highlighting that lower activity does not always result in higher selectivity.

Mechanistic aspects: The obtained results clearly indicate that, whereas home-prepared rutile (HP333) made at low temperature gave rise only to aldehyde and CO_2 for oxidation of both aromatic alcohols, the commercial catalysts and the calcined home-prepared ones yielded a very unselective reaction, with the formation of hydroxylated aldehydes and open-ring products detected during BA oxidation, besides aldehyde and CO_2.



Scheme 1. Proposed reaction schemes (it should be considered that all the aromatic compounds reported in the scheme can undergo direct mineralisation to CO_2). R = H, OCH_3.

The selectivity results of the oxidation of alcohol to aldehyde are surprisingly high (up to 60% for MBA; the highest value previously reported for MBA was 41%), and they were found by using a home-prepared anatase catalyst.[15] It should be considered that the reaction takes place in water without any organic co-solvent. Under these conditions, the solvent represents a highly unselective medium, in which the behaviour of hydroxyl radicals is equally unselective. Instead the features of the synthesised catalysts allow high selectivity even in this environment.

Table 1 shows how an increase in crystallinity causes a significant decrease in selectivity, if we do not consider the amorphous HP298. This could be ascribed not only to the different crystallinity, but also to a drastic reduction of surface hydroxyl groups, and hence hydrophilicity of samples, occurring upon calcination. A current FTIR investigation we are carrying out is showing how this could determine a greater difficulty for the produced aldehyde to desorb from the catalyst surface to the bulk of solution, thus undergoing further oxidation.

Upon using highly crystalline samples, results of GC–MS analyses have highlighted the presence of the three isomers of hydroxybenzaldehyde, but no presence of hydroxybenzyl alcohol was observed. This could be caused by the much higher ease of transformation of an aromatic alcohol into an aldehyde rather than into hydroxybenzyl alcohol isomers. Moreover, 2,5-dihydroxybenzaldehyde was also detected, but the presence of other isomers obtained from the entrance of a hydroxyl radical at the ring position activated by the first hydroxyl radical can also be hypothesised, following a previously reported general behaviour.[8] These recent results showed that the attack of an OH radical on an aromatic ring takes place in *ortho* and *para* positions when an electron-donor group is present; to the contrary, in its absence all three of the isomers are formed.

Previously reported results for anatase[15] showed that the primary oxidation step of MBA involves in any case either direct mineralisation to CO_2 or formation of an aldehyde. However, no hydroxylated 4-methoxybenzaldehyde isomers were detected. These species were detected in our investigation in trace amounts even when using commercial and highly crystalline (home-prepared) samples.

Scheme 1 shows the hypothesised mechanism for the two alcohols. Both BA and MBA can either undergo direct mineralisation to CO_2 (not shown) through adsorbed intermediates,[15] or be partially oxidised to other aromatic and eventually aliphatic compounds.

The first step (Scheme 1A) of BA and MBA partial oxidation to an aldehyde is the abstraction of an electron in the OH group by a hole (h^+; abstraction from an aromatic ring is indeed much more difficult). Once this rate-determining step has taken place, the subsequent transformations involve the formation of a −CHO group by means of either an electron hole or an OH radical.

In addition, it is worth noting that O_2^- could play a role in producing oxidant species (for instance HO_2 radicals) by reacting with H_2O.

Benzaldehyde, once formed, can be subjected to a further attack of OH radicals on the aromatic ring (Scheme 1, step B). This is the rate-determining step for the production of hydroxylated aromatic compounds through the elimination of a hydrogen atom by means of either an electron hole or an OH radical. All of the monohydroxylated isomers are obtained because an electron-withdrawing group (−CHO) is present (general behaviour previously observed).[8] Analogously, the second hydroxylation can take place in the position activated by the first −OH group.

A different fate for benzaldehyde can be oxidation to benzoic acid by means of hydrogen-atom abstraction from the aldehydic carbon atom, with formation of an acyl radical (Scheme 1, step B). Two possibilities of how this occurs could be 1) an electron transfer to an acyl cation followed by the attack of a water molecule as depicted in Scheme 1, or 2) a cross-dimerisation with an OH radical. Considering that the concentration of these two different radicals should be rather low, we prefer the first hypothesis.

4-Methoxybenzaldehyde, on the other hand, is only subjected to direct mineralisation, because neither hydroxylated species nor acid were formed in detectable amounts when using catalysts prepared at low temperature.

The presence of hydroxylated aldehydes (step B), detected only from BA and with the most crystalline catalysts, suggests that the higher oxidising power of these samples can allow the hydroxylation reaction, which decreases the selectivity towards aldehyde. So the mild oxidising power of HP333 gives rise to a high selectivity, due to the greater difficulty of hydroxylating the obtained aldehyde or directly breaking the aromatic ring.

Selectivity towards aldehyde, reaction rate and intermediates were found to be very different for BA and MBA. This could be ascribed to the presence of an electron-donor group, such as methoxy, in the *para* position of MBA. The significantly higher reaction rate of MBA can be ascribed to a much easier abstraction of a hydrogen atom by a hole (h^+) due to the presence of a methoxy group because it increases the delocalisation on the ring. This donor group could be effective as a hole trap because it contains an oxygen atom and can stabilise the aromatic ring, thus increasing the selectivity towards aldehyde. Regarding this transformation, it was found in the literature that electron transfers in the gas phase and in solution occur from the oxygen atom of the benzylic alcohol and this transfer is easier for MBA than BA.[17]

The presence of some amounts of benzoic acid on the one hand, and the absence of *p*-methoxybenzoic acid (for conversion $<80\,\%$) on the other suggest that electron-donor groups inhibit the formation of aromatic acid, as previously reported.[18]

The different amount of CO_2 produced from BA and MBA could also be attributed to the very different solubility of benzaldehyde and 4-methoxybenzaldehyde in water (100 vs. 4290 $mg\,L^{-1}$ at 293 K, respectively). Desorption of benzaldehyde from the catalyst surface after its formation can therefore be prevented by its hydrophobic character, so that either a subsequent hydroxylation or mineralisation to CO_2 would be favoured.

Conclusion

In conclusion, the oxidation of two aromatic alcohols in water has been reported, and selectivity towards aldehyde was shown to be significantly higher for home-prepared rutile TiO_2 made at low temperature (HP333) relative to other home-prepared and commercial highly crystalline catalysts. The obtained selectivity was three- to sevenfold higher for both alcohols, and no byproducts were found when working with HP333, with the exception of CO_2. Highly crystalline samples displayed, conversely, a low selectivity and in the case of BA gave hydroxylated byproducts and aromatic acid. The very different selectivities (60 and 38 % for MBA and BA, respectively) were justified by considering the presence of an electron-donor group in the former case and the hydrophobic nature of benzaldehyde.

The mild experimental conditions used, consisting of aqueous suspensions free of any organic co-solvents, and the absence of heavy metals, high temperatures or pressures, allow us to propose this process as a green route for partial oxidation of alcohols.

Experimental Section

Preparation of home-prepared TiO_2 catalysts: The precursor solution was obtained by slowly adding $TiCl_4$ (20 mL, >97 %, Fluka) dropwise into a 2 L beaker containing water (1 L) under agitation because the hydrolysis of $TiCl_4$ is a highly exothermic reaction producing significant amounts of HCl vapour. The addition had a total duration of 5 min. After magnetic mixing (450 rpm) for 10 min, the resulting solution was kept in a closed oven for 2 d at 333 K. Then a white suspension was obtained. Drying was carried out at 333 K by means of a rotary evaporator (Büchi Rotavapor M) working at 50 rpm to eventually obtain the powdered catalyst (HP333). To check the influence of the degree of crystallinity, HP333 was calcined at 673 and 973 K for 6 h. The obtained samples were named HP673 and HP973, respectively. Another sample (HP333D) was prepared by dialysing HP333 by using a dialysis tubing cellulose membrane (average flat width = 76 mm, 12 400 MW cut-off pores, Aldrich) for approximately 3 d, changing the distilled water every 8 h (5 L) until the conductivity value of water was found to be negligible. An amorphous TiO_2 powder (HP298) was also prepared by following the hereafter described procedure. $TiCl_4$ (2.5 mL) was added dropwise into a 100 mL beaker containing water (25 mL). During the addition, which lasted 5 min, the solution was magnetically stirred at 450 rpm. Upon closing the beaker and mixing the solution for 12 h at room temperature, a clear solution was eventually obtained. Afterwards the prepared solution was added to 1 M NaOH (90 mL) under magnetic agitation. The resulting suspension was filtered and washed until the washing water was found to have a neutral pH and a negligible conductivity.

Photocatalytic experimental procedure: A cylindrical Pyrex batch photoreactor with immersed lamp, containing the aqueous suspension (0.5 L), was used to perform the reactivity experiments. The initial alcohol concentration was approximately 1 mM. The photoreactor was provided with ports in its upper section for the oxygen inlet and outlet and for sampling. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the homogeneity of the reacting mixture. A scheme of the reactor can be seen in ref. [8b]. A medium-pressure Hg lamp (125 W, Helios Italquartz, Italy) axially positioned within the photoreactor was cooled by water circulating through a Pyrex thimble; the temperature of the suspension was about 300 K. The radiation energy impinging on the suspension had an average value of 10 $mW\,cm^{-2}$. It was measured by using a UVX digital radiometer at $\lambda = 360$ nm. Before switching on the lamp, oxygen was bubbled into the suspension for 30 min at room temperature to reach the thermodynamic equilibrium. Adsorption of the alcohols in the dark was always quite low, less than 3 %. Liquid samples (containing suspended catalyst powder) were taken at fixed time intervals and filtered through a 0.45 μm hydrophilic membrane (HA, Millipore) before being analysed. An aqueous solution of 1 M NaOH was used to adjust the initial pH to seven for the performed runs. All of the chemicals used were purchased from Sigma-Aldrich with a purity of >98 %.

Analytical techniques: The quantitative determination and identification of the species present in the reacting suspension was performed by means of a Beckman Coulter HPLC instrument (System Gold 126 solvent module and 168 diode array detector) equipped with a Luna 5 μm phenyl–hexyl column (250 mm long × 2 mm i.d.) and 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 and 65 % 40 mM KH_2PO_4 aqueous solution. TOC analyses were carried out by using a 5000 A Shimadzu TOC analyser. GC–MS analyses were performed by means of a GC–MS Perkin–Elmer Turbomass and an Autosystem XL chromatograph; a SGE BPX5 capillary column (25 m × 0.22 mm i.d.) was used. The injected solution was prepared by following the subsequent procedure: the reaction suspension (100 mL) was filtered and extraction was carried out by using diethyl ether (20 mL); afterwards the organic phase was concentrated 20 times. XRD patterns of the powders were recorded by using a Philips diffractometer using the $Cu_{K\alpha}$ radiation and a 2θ scan rate of $1.28^\circ\,min^{-1}$. SEM images were obtained by using a microscope (Philips XL30 ESEM) 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 using the single-point BET method using a Micromeritics Flow Sorb 2300 apparatus.

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[1] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.

[2] a) *Photocatalysis and Environment: Trends and Applications* (Ed.: M. Schiavello), Kluwer, Dordrecht, **1988**; b) M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96; c) V. Augugliaro, M. Litter, L. Palmisano, J. Soria, *J. Photochem. Photobiol. C* **2006**, *7*, 127–144; d) L. Zang, W. Macyk, C. Lange, W. F. Maier, C. Antonius, D. Meissner, H. Kisch, *Chem. Eur. J.* **2000**, *6*, 379–384.

[3] a) A. Sclafani, L. Palmisano, M. Schiavello, *J. Phys. Chem.* **1990**, *94*, 829–832; b) M. Addamo, V. Augugliaro, A. Di Paola, E. García-López, V. Loddo, G. Marci, R. Molinari, L. Palmisano, M. Schiavello, *J. Phys. Chem.* B **2004**, *108*, 3303–3310, and references therein.

[4] a) M. Nag, P. Basak, S. V. Manorama, *Mater. Res. Bull.* **2007**, *42*, 1691–1704; b) S. Yin, R. Li, Q. He, T. Sato, *Mater. Chem. Phys.* **2002**, *75*, 76–80; c) L. Li, J. Liu, Z. Jia, *Mater. Lett.* **2006**, *60*, 1753–1757.

[5] a) A. Mills, S. Le Hunte, *J. Photochem. Photobiol. A* **1997**, *108*, 1–35; b) H. Kisch, *Adv. Photochem.* **2001**, *26*, 93–143; c) G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* **2007**, 3425–3437.

[6] a) H. Yoshida, C. Murata, T. Hattori, *Chem. Commun.* **1999**, 1551–1552; b) K. V. Subba Rao, M. Subrahmanyam, *Photochem. Photobiol. Sci.* **2002**, *1*, 597–599; c) A. Maldotti, R. Amadelli, L. Samiolo, A. Molinari, A. Penoni, S. Tollari, S. Cenini, *Chem. Commun.* **2005**, 1749–1751.

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

[8] a) G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, E. García-López, V. Loddo, L. Palmisano, *Chem. Commun.* **2006**, 1012–1014; b) G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, A. Di Paola, E. García-López, V. Loddo, G. Marcì, L. Palmisano, M. Schiavello, *Catal. Today* **2007**, *122*, 118–127.

[9] F. Soana, M. Sturini, L. Cermenati, A. Albini, *J. Chem. Soc. Perkin Trans. 2* **2000**, 699–704.

[10] T. Caronna, C. Gambarotti, L. Palmisano, C. Punta, F. Recupero, *J. Photochem. Photobiol. A* **2005**, *171*, 237–242.

[11] B. Ohtani, S. Tsuru, S.-I. Nishimoto, T. Kagiya, K. Izawa, *J. Org. Chem.* **1990**, *55*, 5551–5553.

[12] a) K. Yamaguchi, N. Mizuno, *Angew. Chem.* **2002**, *114*, 4720–4724; *Angew. Chem. Int. Ed.* **2002**, *41*, 4538–4542; b) G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639.

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

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

[15] G. Palmisano, S. Yurdakal, V. Augugliaro, V. Loddo, L. Palmisano, *Adv. Synth. Catal.* **2007**, *349*, 964–970.

[16] C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, *Langmuir* **2000**, *16*, 2632–2641.

[17] A. J. McEvoy, M. Grätzel, *Sol. Energy Mater. Sol. Cells* **1994**, *32*, 221–227.

[18] E. Baciocchi, M. Bietti, B. Chiavarino, M. E. Crestoni, S. Fornarini, *Chem. Eur. J.* **2002**, *8*, 532–537.

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