Home-prepared anatase, rutile, and brookite TiO_2 for selective photocatalytic oxidation of 4-methoxybenzyl alcohol in water: reactivity and ATR-FTIR study†‡

Vincenzo Augugliaro,*[a] Vittorio Loddo,[a] María José López-Muñoz,[b] Carlos Márquez-Álvarez,[c] Giovanni Palmisano,[a] Leonardo Palmisano*[a] and Sedat Yurdakal[a,d]

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TiO_2 catalysts of anatase, rutile and brookite phase were prepared at low temperature and tested for carrying out the photocatalytic partial oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde (*p*-anisaldehyde) in organic-free water suspensions. Traces of 4-methoxybenzoic acid and open-ring products were the only by-products present, CO_2 being the other main oxidation product. Rutile exhibited the highest yield to *p*-anisaldehyde (62% mol) at a rate of the same order of magnitude of that showed by the other samples. Commercial rutile and anatase photocatalysts were also used for the sake of comparison. The samples have been characterised by an *in situ* ATR-FTIR investigation carried out in conditions simulating the photoreaction ones.

1. Introduction

The selective oxidation of alcohols to their corresponding carbonyl compounds (aldehydes, carboxylic acids and ketones) is a reaction frequently encountered in the synthesis of fine chemicals.[1] Traditional methods for performing such partial oxidations involve the use of 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.[2]

The utilization of radiation to initiate chemical reactions is the principle on which heterogeneous photocatalysis is based. This method is being successfully applied to oxidise harmful molecules on the basis of the generally accepted statement that this advanced oxidation process is quite unselective.[3] Photocatalytic-selective reactions for synthetic purposes are not as common as degradations but have been carried out,[4] although they have been mainly performed either in organic solvents or in the gas phase.[5] Hydrocarbon oxidation,[6] aromatic hydroxylation,[7] naphthalene oxygenation,[8] heterocycle functionalisation[9] and cyclisation of amino acids[10] are some of the few studies related to the selectivity of photocatalytic reactions in water.

Recent results have however highlighted that photocatalysis is also able to perform partial oxidation reactions.[11] In this work home-prepared samples of only anatase, rutile and brookite TiO_2 (hereafter referred to as HPA, HPR and HPB, respectively) have been used for carrying out the partial oxidation of 4-methoxybenzyl alcohol (MBA) to *p*-anisaldehyde (PAA) in aqueous suspension at room temperature. For the sake of comparison also commercial anatase and rutile catalysts were tested. The catalysts have been characterised by their photoactivity and by an *in situ* ATR-FTIR investigation performed in conditions simulating those used during the photoreaction.

2 Experimental

2.1 Catalysts preparation

For the preparation of anatase sample[11b] a precursor solution was obtained by slowly adding 5 mL of $TiCl_4$ drop by drop into a 200 mL beaker containing 50 mL of doubly-distilled water. Since the hydrolysis of $TiCl_4$ is a highly exothermic reaction producing significant amounts of HCl vapours, the $TiCl_4$ addition was performed by vigorously mixing the solution by means of a magnetic stirrer. 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 warming of the solution at the constant temperature of 373 K; the duration of the warming was 0.5 h obtaining a white suspension at the end of treatment. The suspension was then dried at 323 K by means of a rotary evaporator apparatus (model Buchi Rotovapor M) working at 50 rpm in order to obtain the final HPA powdered catalyst.

[a]*"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università degli Studi di Palermo, Viale delle Scienze, 90128, Palermo, Italy. E-mail: augugliaro@dicpm.unipa.it, palmisano@dicpm.unipa.it; Fax: +3909123863750; Tel: +3909123863722*
[b]*Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, C/Tulipán s/n, 28933, Móstoles, Madrid, Spain*
[c]*Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, 28049, Cantoblanco, Madrid, Spain*
[d]*Kimya Bölümü, Fen Fakültesi, Anadolu Üniversitesi, Yunus Emre Kampüsü, 26470, Eskişehir, Turkey*

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For the preparation of rutile sample[11c] the precursor solution was obtained by slowly adding dropwise 20 mL of $TiCl_4$ to a 2 L beaker containing 1 L of doubly-distilled water under continuous mixing. The addition had a total duration of 5 min. After mixing for 10 min, the beaker containing the sol was sealed and kept in an oven for 2 days at 333 K. Then the resulting suspension was dried at 333 K by means of the rotary evaporator machine, in order to obtain the final HPR powdered catalyst.

For the preparation of brookite sample[11d] $TiCl_4$ was added dropwise to an aqueous HCl solution, under stirring at room temperature. The volume ratios among $TiCl_4$, HCl and H_2O were 1 : 16 : 42, respectively. By testing different ratios, it was found that the produced dispersions were more opalescent by decreasing the HCl concentration. After continuous stirring of 2 h a clear transparent solution was obtained. Then the solution was boiled with constant stirring in a standard reflux apparatus for 2 days obtaining a suspension of pure brookite and rutile nanoparticles. Brookite particles were separated by peptization from the brookite–rutile suspension. In fact, when the pH of the suspension is higher than 0.8, brookite particles settle very slowly while rutile particles easily precipitate. On these grounds, time was allowed for the settling of rutile particles and therefore the supernatant milky suspension was removed and stored. Then water was added to the remaining precipitate, restoring the initial liquid volume. The separation of supernatant from the precipitate was repeated several times till a transparent liquid covered the solid rutile. The dispersion containing the brookite particles was dried at 328 K by means of the rotary evaporator machine.

2.2 Photocatalytic experimental procedure

A cylindrical Pyrex batch photoreactor with immersed lamp, containing 0.5 L of aqueous suspension, was used to perform the reactivity experiments. Initial alcohol concentrations were 1 and 10 mM. The 10 mM concentration has been used to study the variation in selectivity and with scaling up aims. The same amount of catalyst (0.4 g L^{-1}) was used for all the runs; that amount guaranteed that nearly all the photons emitted by the lamp were absorbed by the suspension. Besides the HPA, HPR and HPB catalysts, commercial anatase (Merck) and rutile (Sigma Aldrich, SA) TiO_2 have been tested for comparison. The photoreactor was provided with ports in its upper section for the inlet and outlet of oxygen and for sampling. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the homogeneity of the reacting mixture. A 125 W medium pressure Hg lamp (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 radiometer UVX Digital, at 360 nm.

Before switching on the lamp, oxygen was bubbled into the solution 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 were filtered through a 0.45 μm hydrophilic membrane (HA, Millipore) before being analysed. NaOH 1M solution was used to adjust the initial pH to 7 for all the performed runs.

2.3 Analytical techniques

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 5 μ 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. 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 1.28° per 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 deposited. BET specific surface areas were measured by the single-point BET method using a Micromeritics Flow Sorb 2300 apparatus. All the used chemicals were purchased from Sigma Aldrich with a purity >99.0%.

2.4 *In situ* ATR-FTIR measurements

Infrared spectra of thin films of the photocatalysts were recorded using a Thermo Nicolet Nexus FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector and a horizontal ATR accessory (SensIR Technologies DurasamplIR, 9-reflection diamond-faced ZnSe prism). Titania samples ground in an agate mortar were suspended in Milli-Q deionized water (25 mg solid in 25 mL water) and sonicated for 20 min (Elma Transsonic T470/H ultrasonic cleaning unit). Thin films were prepared by dropping 50 μL of the suspension onto the ATR crystal and then allowing the solvent to evaporate. The procedure was repeated three times to obtain thin films containing *ca.* 150 μg TiO_2. A 100 mL volume glass flow cell was attached to the ATR plate through an o-ring sealed connection and the thin film was dried at room temperature for several minutes in a stream of synthetic air (Air Liquide, Alphagaz Air 1). Adsorption of water and MBA (Sigma Aldrich, 98%) vapours on the dried TiO_2 thin films was carried out at room temperature under static conditions by introducing 0.2 mL of each liquid adsorbate inside the closed glass cell previously purged with synthetic air. After adsorption in the dark for around 80 min, UV irradiation of the photocatalyst films in contact with the water/alcohol-saturated air atmosphere was performed using an 80 W mercury vapour lamp (OSRAM HQL de luxe MBF-U). The UV lamp was turned on 2 min before exposing the photocatalyst to the light in order to allow the lamp to reach full power. The light was filtered by passing through a Pyrex vessel containing a 0.1 M $CuSO_4$ aqueous solution. Time-resolved FTIR spectra in the 4000–900 cm^{-1} wavenumber range, with a resolution of 4 cm^{-1}, were recorded along the adsorption and irradiation steps at room temperature. Each spectrum was obtained by averaging 10 scans accumulated in 4 s. Happ-Genzel apodization function was applied. The spectra were referenced against the spectrum of the dried TiO_2 thin film. FTIR spectra of MBA and PAA were recorded as references by depositing directly the liquid specimens (Sigma Aldrich, 98%) on the bare ATR crystal.

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Table 1 BET specific surface areas (SSA) of catalysts and their performance for the photocatalytic oxidation of 4-methoxybenzyl alcohol (MBA) to *p*-anisaldehyde. Photoreaction half time, $t_{\frac{1}{2}}$, and selectivity values have been obtained by using 0.4 g L^{-1} catalyst

Catalysts	SSA/ m^2 g^{-1}	Crystallite size/nm	Particle size/nm	MBA/ mM	$t_{1/2}$/h	Selectivity (%mol)
HPA[a]	235	5	28	1	4.1	31
HPA[a]	235	5	28	10	19.5	39
HPR[b]	107	7	50	1	2.1	58
HPR[b]	107	7	50	10	8.8	62
HPB[c]	82	9	95	1	1.8	39
HPB[c]	82	9	95	10	9.1	50
SA[d]	2.5	52	240	1	2.1	21
Merck[e]	10	60	170	1	2.0	16

[a] Home-prepared anatase, [b] Home-prepared rutile, [c] Home-prepared brookite, [d] Sigma-Aldrich rutile. [e] Anatase.

3. Results and discussion

3.1 Catalyst characterization

All the information obtained by the textural characterisation of catalysts is summarised in Table 1. XRD patterns (reported in the ESI‡) indicate the presence of only one phase for each catalyst, *i.e.* anatase, rutile or brookite. The crystallite sizes, as obtained from Scherrer's equation, were in the 5–9 nm range for HP catalysts, whereas the dimension of crystallites was 52 nm for SA TiO_2 and 60 nm for Merck TiO_2. BET specific surface areas were found in the 82–235 m^2 g^{-1} range with the exception of SA and Merck which exhibited much lower values (2.5 and 10 m^2 g^{-1}, respectively). All the home prepared samples were shown to be mesoporous. SEM images (reported in the ESI‡) showed that the catalysts consist of agglomerates. The average diameters of the agglomerates were *ca.* 28, 50, 95, 240, and 170 nm for HPA, HPR, HPB, SA, and Merck respectively.

The catalyst characterization shows that in the HP catalysts crystallite sizes and particle sizes increase in the following order: anatase < rutile< brookite; this feature corresponding to surface area values following the inverse order.

3.2 Photoreactivity

Preliminary runs were carried out in the absence of catalyst; after irradiating the alcohol solution (initial concentration of 1 mM) for 12 h, a very low alcohol conversion (only 32.4%) was measured with an overall yield in aldehyde of 30.8% mol. It was also verified that in the presence of catalyst no reactions took place in the dark.

The reactivity results in the presence of irradiated catalysts clearly indicate that the MBA photocatalytic oxidation proceeds through two parallel reaction routes active since the start of irradiation: the first one determines the MBA partial oxidation to PAA while the second one eventually causes the direct mineralization of MBA to CO_2. This last pathway occurs through a series of reactions taking place over the catalyst surface and producing intermediates not desorbing to the bulk of solution. The carbon balance for HP samples, verified by taking into account the unreacted alcohol, the produced aldehyde and CO_2, was always higher than 95%. The small loss may be ascribed to the production of open-ring compounds coming from over-oxidation of aldehyde. Table 1 summarizes the photoreactivity results obtained with the home prepared catalysts and two commercial TiO_2 samples, one pure rutile and the other pure anatase. The catalyst performance is quantified by the photoreaction half time, $t_{\frac{1}{2}}$, and the corresponding selectivity.

The highest selectivity is shown by the HPR sample and the lowest one by commercial anatase. The increase of initial MBA concentration favourably affects the selectivity of all HP catalysts. The reaction rates of HPB, HPR and commercial samples are all of the same order of magnitude and higher than that of HPA, which however shows the highest specific surface area. The Degussa P25 TiO_2 was also tested (powder amount: 0.4 g L^{-1}; initial alcohol concentration: 1 mM); this catalyst, which is a mixture of anatase and rutile, showed the highest photoreactivity ($t_{\frac{1}{2}}$ = 0.72 h) but also the lowest selectivity (8% mol) thus confirming that it is the best catalyst for complete photodegradation of organic compounds but not useful for partial oxidation reactions.

As to concern over the influence of MBA concentration on the photoreaction half time, the finding that the $t_{\frac{1}{2}}$ values depend on the initial alcohol concentration indicates that the degradation rate does not follow a first order kinetics. On this ground an empirical kinetics of *n* order with respect to MBA concentration has been fitted to the $t_{\frac{1}{2}}$ values obtained for each catalyst at the two used MBA concentrations. The empirical *n* order is given by the following relationship:

$$n = 1 + \frac{\log\left[(t_{\frac{1}{2}})_1/(t_{\frac{1}{2}})_2\right]}{\log\left[C_2/C_1\right]} \quad (1)$$

in which the subscripts refer to the different concentrations. The calculated values of *n* are 0.32, 0.30, and 0.38 for HPA, HPR, and HPB, respectively, suggesting that the kinetics of MBA degradation on pure brookite catalyst is more sensitive to MBA concentration.

The dependence of reaction rate on the MBA concentration has been reported[12] to be of Langmuir type; in this case the reaction kinetics is of zero order at high MBA concentrations and of first order at low ones. The values of *n* are in the 0–1 range indicating that in the course of photoprocess the MBA degradation kinetics turns from zero to one order.

3.3 ATR-FTIR investigations

Fig. 1–4 show the *in situ* ATR-FTIR spectra of HPA, HPR, HPB and SA samples, acquired when exposing the samples in an atmosphere of synthetic air saturated with MBA and water, followed by irradiation.

It was observed, in all cases upon contact of titania with the aromatic alcohol and water in the dark, an enhancement over time in the intensity of the absorption band centred at 1640 cm^{-1} due to the bending vibration mode of adsorbed molecular water, concomitant to the growth of bands at 1614, 1515, 1468, 1302, 1247, 1215, 1177, 1111 and 1033 cm^{-1}.

According to the similarity in the wavenumber values of the latter bands to those in pure MBA, they can be ascribed to a non-dissociative adsorption of the alcohol on the titania surface. This appears to be the main way of interaction between MBA and titania as no bands ascribed to alcoholate species were simultaneously

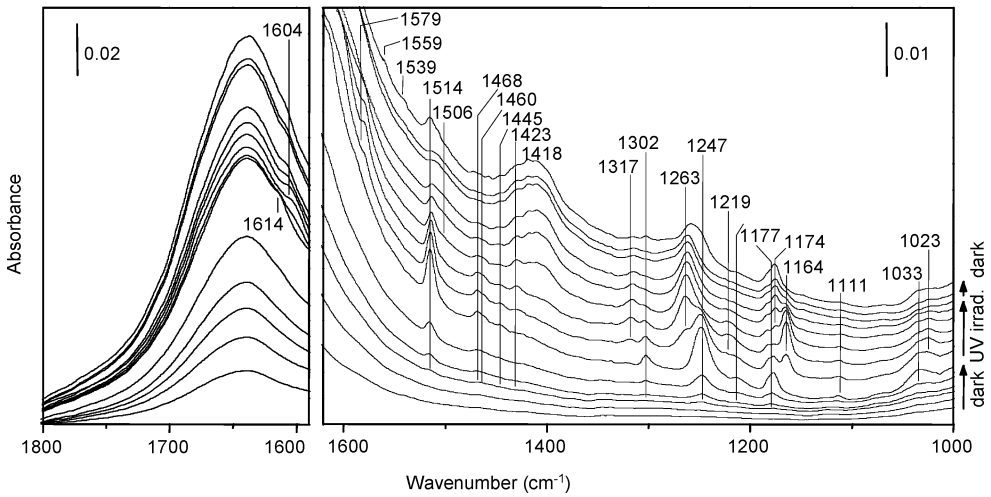


Fig. 1 Selected ATR-FTIR spectra of HPA thin film in contact with a synthetic air atmosphere containing water and 4-methoxybenzyl alcohol vapours. From bottom to top, spectra recorded after adsorption in the dark for 1, 5, 11, 19, 36 and 77 min, subsequent UV irradiation for 1, 3, 7, 11, 17 and 32 min, and again in the dark for 0.5 and 18.5 min. The film was previously exposed to water vapour for 10 min. Spectra have been referenced against the spectrum of the dried photocatalyst.

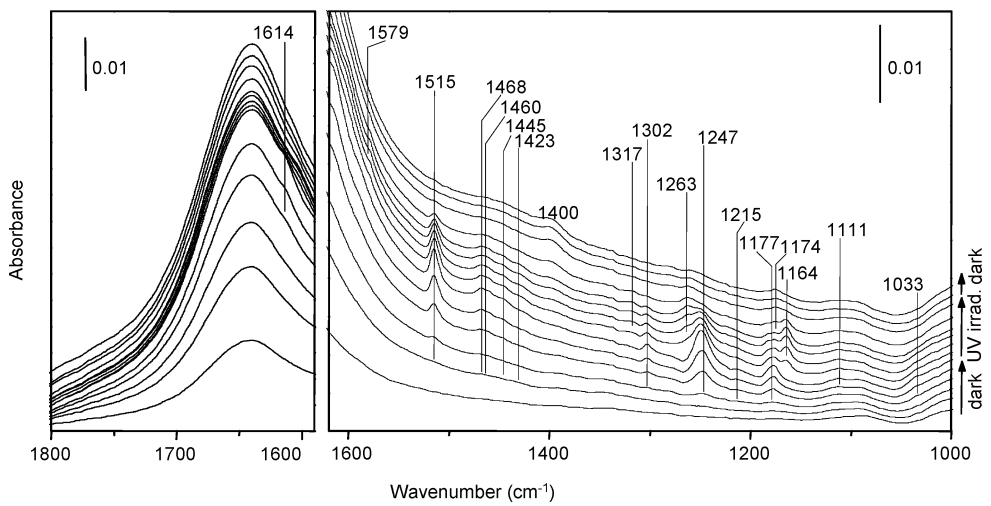


Fig. 2 Selected ATR-FTIR spectra of HPR thin film in contact with a synthetic air atmosphere containing water and 4-methoxybenzyl alcohol vapours. From bottom to top, spectra recorded after adsorption in the dark for 1, 7, 15, 33, 53 and 86 min, subsequent UV irradiation for 1, 2, 3, 4, 8, 15 and 21 min, and again in the dark for 4 min. The film was previously exposed to water vapour for 10 min. Spectra have been referenced against the spectrum of the dried photocatalyst.

detected. Upon irradiation, bands derived from MBA adsorption were greatly reduced in intensity whereas new bands appeared, clearly distinguishable from those of MBA, the most prominent peaked at 1604, 1579, 1317, 1263 and 1164 cm^{-1}. The location of all these bands matches that of the most intense ones observed in the spectrum of pure PAA, and they can be respectively ascribed to C=C stretching, C–C asymmetric stretching, C–O stretching, CH_3 asymmetric deformation and C–H in plane bending vibrations in PAA, according to the assignments made in a recent vibrational spectroscopy investigation using *ab initio* and density functional theory.[13] Even though an absorption band corresponding to the C=O stretching vibration of the aldehyde should be observed at 1665 cm^{-1}, it is not clearly detected in any case as it is overlapped by the strong absorption due to the bending vibration mode of adsorbed molecular water.

For a better comparison of the adsorption and photocatalytic response among the evaluated titania samples, the profiles showing the time evolution of the amounts of adsorbed water, MBA and PAA are displayed in Fig. 5. The data are plotted as the integrated absorbance of selected IR bands for each species. It should be noticed that the low surface area of sample SA accounts for the notably lower intensity of bands due to adsorbed species as compared with HP samples. As can be observed, the relative amounts of adsorbed alcohol and molecular water evidence a distinctively lower hydrophilicity of the commercial rutile as compared to all HP samples, among which HPB exhibits the highest hydrophilicity. Nevertheless, it is noticeable from the continuous increase of adsorbed MBA in the presence of water that there is not a competition for adsorption sites between both molecules. In a previous work[14] it was found that, in the case

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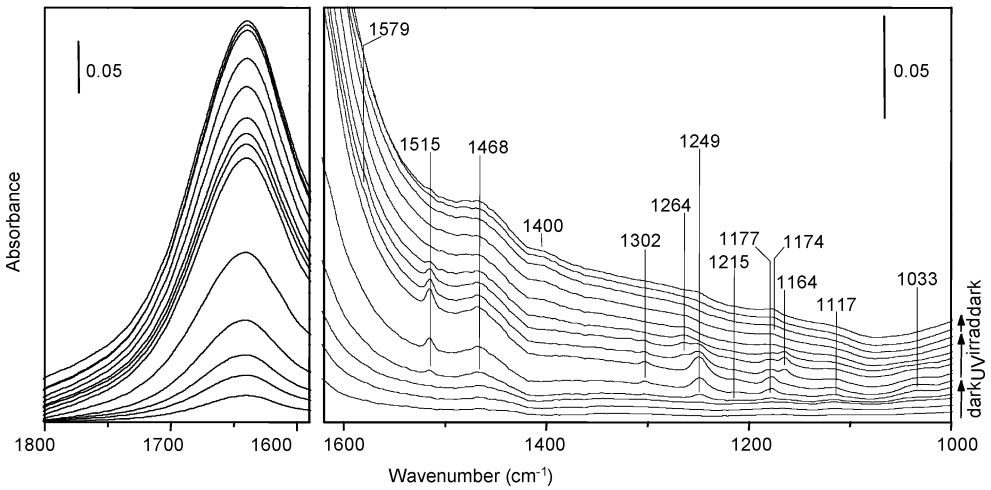


Fig. 3 Selected ATR-FTIR spectra of HPB thin film in contact with a synthetic air atmosphere containing water and 4-methoxybenzyl alcohol vapours. From bottom to top, spectra recorded after adsorption in the dark for 1, 4, 8, 21, 45 and 76 min, subsequent UV irradiation for 1, 2, 4, 9, 17 and 30 min, and again in the dark for 6 and 15 min. The film was previously exposed to water vapour for 10 min. Spectra have been referenced against the spectrum of the dried photocatalyst.

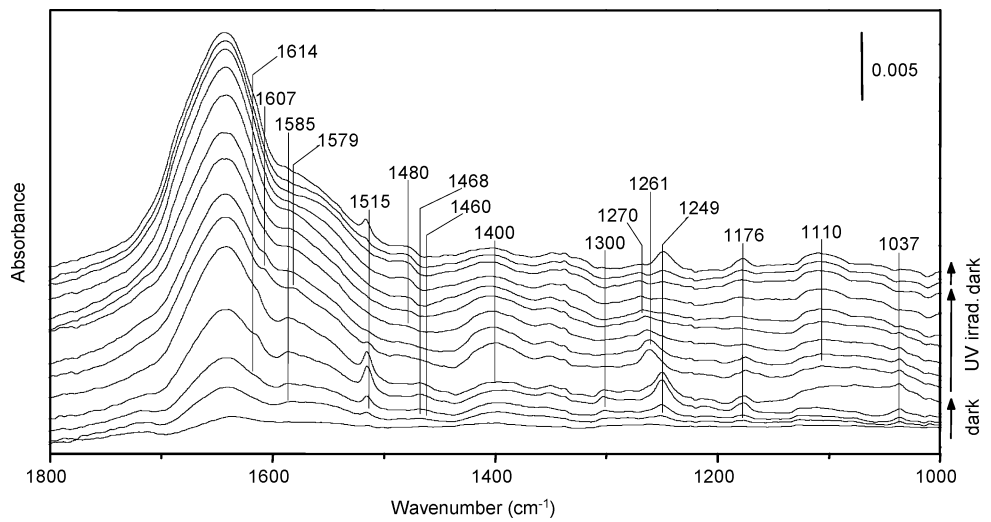


Fig. 4 Selected ATR-FTIR spectra of SA thin film in contact with a synthetic air atmosphere containing water and 4-methoxybenzyl alcohol vapours. From bottom to top, spectra recorded after adsorption in the dark for 1, 7, 13, 39 and 77 min, subsequent UV irradiation for 0.5, 1.5, 3.5, 6, 13, 23 and 30 min, and again in the dark for 3 and 10 min. The film was previously exposed to water vapour for 10 min. Spectra have been referenced against the spectrum of the dried photocatalyst.

of benzyl alcohol (BA) adsorption on the HPA sample, water favourably competed with BA therefore determining a partial displacement of BA from the TiO_2 surface. On the basis of the reaction results, it was proposed that water competed with BA molecules for the adsorption on mineralization sites, thus accounting for the high selectivity to benzaldehyde observed in this sample. The differences found in the present work for MBA adsorption in comparison to BA can be related to the electron-donating character of the methoxy group, able to increase the electron density of the aromatic ring and therefore favouring a stronger adsorption of the alcohol on the titania surface. As a consequence, MBA molecules are not easily displaced by water molecules during co-adsorption in the dark, in contrast with the results obtained for BA. Accordingly, the fact that water molecules do not seem to significantly affect the adsorption of MBA on the titania surface can explain that, in this case, there is no direct correlation between hydrophilicity of the surface and the observed selectivity to the photocatalytic formation of PAA.

It can also be observed in Fig. 5 that upon irradiation the intensity of adsorbed MBA decreased whereas PAA bands grew quickly in the first few minutes and showed subsequently a progressive decrease. When UV irradiation was stopped, the remaining bands ascribed to aldehyde quickly disappeared, while those due to adsorbed MBA started to grow slowly. Therefore, the time-resolved ATR-FTIR experiments allow one to conclude that UV irradiation promotes a fast oxidation of MBA and hinders its adsorption on the titania surface, which eventually results in a virtually nil steady-state surface coverage by the alcohol during the photocatalytic reaction. In all cases, irradiation of the samples produces also an enhancement of the water adsorption, as shown

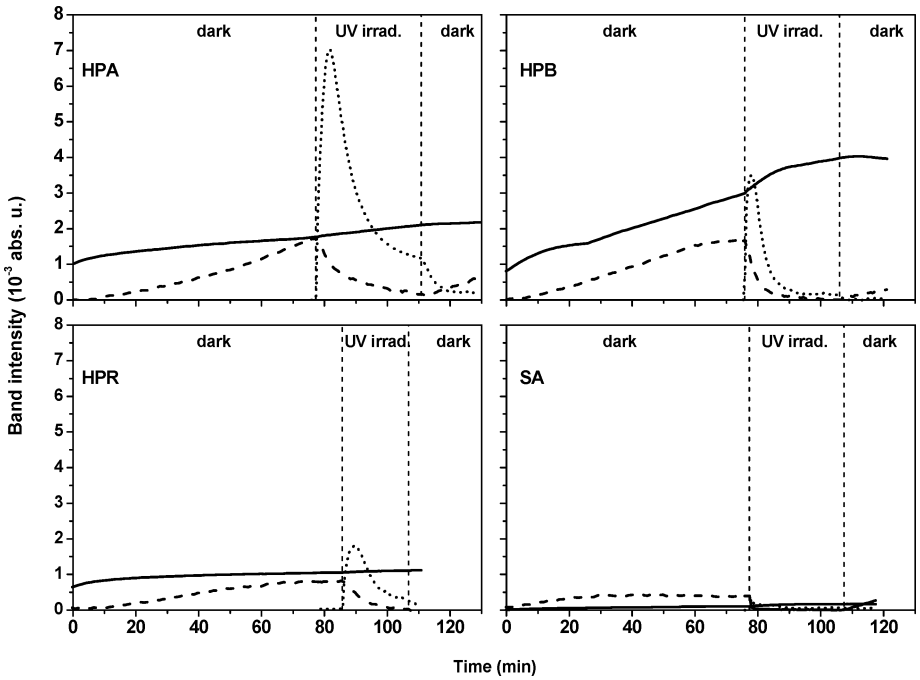


Fig. 5 Time-dependent intensity of selected IR bands representative of water (full line), 4-methoxybenzyl alcohol (dashed line) and *p*-anisaldehyde (dotted line) adsorbed on titania thin films in contact with a synthetic air atmosphere containing water and 4-methoxybenzyl alcohol vapours in the dark, under UV irradiation and after switching off the lamp.

by the increase of the rate of growth of the band due to adsorbed water. This effect, which disappears as the UV irradiation ends, is most pronounced for sample HPB, thus providing further evidence of the higher hydrophilicity exhibited by this sample.

It is worthy to note that in the different HP samples, the maximum intensity reached by the PAA bands in the spectra recorded during irradiation is related to the selectivity to aldehyde exhibited by the titania specimen in the photocatalytic oxidation of MBA. The higher the amount of PAA adsorbed on the titania surface, the lower the selectivity. This can be explained by considering that a stronger adsorption of the aldehyde on the surface would favour its subsequent reaction to further oxidized products. Indeed, under irradiation, in the infrared spectra of sample HPA, the one which exhibits the lowest selectivity, it can be observed a continuous growth of a group of overlapped absorption bands in the 1420–1400 cm^{-1} range, together with weak shoulders at 1539 and 1559 cm^{-1}, indicative of products derived from the oxidation of the aldehyde. The species characterized by these bands seem to remain strongly adsorbed on the titania surface, as their band intensities are not modified with time after switching off the lamp. On the other hand, although the broad band at *ca.* 1400 cm^{-1} also develops under irradiation of samples HPR and HPB, it shows much weaker intensity in agreement with the higher selectivity exhibited by these samples.

4. Conclusions

Anatase, rutile and brookite TiO_2 catalysts, home prepared with a simple procedure without calcination treatment, have been successfully used for carrying out the partial oxidation of an aromatic alcohol, MBA, to the corresponding aldehyde. The selectivity values shown by these catalysts are two or three times higher than those of the corresponding commercial specimens, the oxidation rate being comparable. The rutile sample shows the highest selectivity. The ATR-FTIR investigation, aimed at obtaining likely explanations of the photoreactivity results, gives interesting information even if care must be used in correlating it with the photoactivity. The spectral data show that the main way of interaction between MBA and titania surface in the dark is a non-dissociative adsorption of the alcohol. Under UV irradiation, the main product detected on the photocatalyst's surface is the aldehyde (PAA). Substantial differences in the maximum intensity reached by the PAA bands in the spectra recorded during irradiation are observed among the HP samples. These results are related to the selectivity to aldehyde exhibited by the different titania specimens in the photocatalytic oxidation of MBA. When the amount of PAA adsorbed on the titania surface increases the selectivity decreases, suggesting that a stronger adsorption of the aldehyde on the surface favours its subsequent reaction to further oxidized products. All the HP catalysts are much more hydrophilic than the commercial ones. The finding that there is no competition for adsorption sites between water and MBA molecules can be explained by considering that the alcohol exhibits a strong adsorption on the titania surface. This adsorption is likely favoured by the electron-donating character of the MBA methoxy group, able to increase the electron density of the aromatic ring, and therefore MBA molecules are not easily displaced by water molecules. Under irradiation, for HPA catalyst the products derived from the oxidation of the aldehyde remain strongly adsorbed on the titania surface while for HPR and HPB samples the interaction is much weaker in agreement with the higher selectivity exhibited by these samples.

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Notes and references

1 B. M. Trost, I. Fleming, and S. V. Ley, (Eds.), *Comprehensive Organic Synthesis*, vol. 7, Pergamon Press, Oxford, 1991.

2 (*a*) G. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636; (*b*) R. A. Sheldon, I. W. C. E. Arends, G. ten Brink and A. Dijksman, *Acc. Chem. Res.*, 2002, **35**, 774; (*c*) 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 and G. J. Hutchings, *Science*, 2006, **311**, 362; (*d*) C. Li and L. Chen, *Chem. Soc. Rev.*, 2006, **35**, 68; (*e*) K. Ohkubo, K. Suga and S. Fukuzumi, *Chem. Commun.*, 2006, **19**, 2018.

3 M. Schiavello, (Ed.), *Heterogeneous Photocatalysis*, Wiley, Chichester, 1997.

4 (*a*) G. Palmisano, V. Augugliaro, M. Pagliaro and L. Palmisano, *Chem. Commun.*, 2007, 3425; (*b*) H. Kisch, *Adv. Photochem.*, 2001, **26**, 93.

5 (*a*) K. V. Subba Rao and M. Subrahmanyam, *Photochem. Photobiol. Sci.*, 2002, **1**, 597; (*b*) A. Maldotti, R. Amadelli, L. Samiolo, A. Molinari, A. Penoni, S. Tollari and S. Cenini, *Chem. Commun.*, 2005, 1749.

6 M. A. Gonzalez, S. G. Howell and S. K. Sikdar, *J. Catal.*, 1999, **183**, 159.

7 (*a*) G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, E. García-López, V. Loddo and L. Palmisano, *Chem. Commun.*, 2006, 1012; (*b*) G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, A. Di Paola, E. García-López, V. Loddo, G. Marcì, L. Palmisano and M. Schiavello, *Catal. Today*, 2007, **122**, 118.

8 F. Soana, M. Sturini, L. Cermenati and A. Albini, *J. Chem. Soc., Perkin Trans.*, 2000, **2**, 699.

9 T. Caronna, C. Gambarotti, L. Palmisano, C. Punta and F. Recupero, *J. Photochem. Photobiol. A*, 2005, **171**, 237.

10 B. Ohtani, S. Tsuru, S.-I. Nishimoto, T. Kagiya and K. Izawa, *J. Org. Chem.*, 1990, **55**, 5551.

11 (*a*) S. Higashida, A. Harada, R. Kawakatsu, N. Fujiwara and M. Matsumura, *Chem. Commun.*, 2006, 2804; (*b*) G. Palmisano, S. Yurdakal, V. Augugliaro, V. Loddo and L. Palmisano, *Adv. Synth. Catal.*, 2007, **349**, 964; (*c*) S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro and L. Palmisano, *J. Am. Chem. Soc.*, 2008, **130**, 1568; (*d*) A. Di Paola, G. Cufalo, M. Addamo, M. Bellardita, R. Campostrini, M. Ischia, R. Ceccato and L. Palmisano, *Colloids Surf. A*, 2008, **317**, 366.

12 V. Loddo, S. Yurdakal, G. Palmisano, G. E. Imoberdorf, H. A. Irazoqui, O. M. Alfano, V. Augugliaro, H. Berber and L. Palmisano, *Int. J. Chem. Reactor Eng.*, 2007, **5**, A57.

13 S. Gunasekaran, S. Seshadri, S. Muthuc, S. Kumaresan and R. Arunbalaji, *Spectrochim. Acta, Part A*, 2008, **70**, 550.

14 V. Augugliaro, H. Kisch, V. Loddo, M. J. López-Muñoz, C. Márquez-Álvarez, G. Palmisano, L. Palmisano, F. Parrino and S. Yurdakal, *Appl. Catal. A: General*, 2008, **349**, 189.