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Environmentally Friendly Photocatalytic Oxidation of Aromatic Alcohol to Aldehyde in Aqueous Suspension of Brookite TiO_2

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Abstract Photocatalytic oxidation of 4-methoxybenzyl alcohol to aldehyde in water has been achieved by using home-prepared uncalcined brookite TiO_2. Three different lamp irradiances have been applied in order to check the influence of light power on selectivity. Well known commercial samples (Degussa P25 and Merck) have been used for comparison purposes. A maximum selectivity towards aldehyde of ca. 56% (i.e. ca. 3 times higher than that obtained with commercial TiO_2) has been achieved.

Keywords Selective photocatalysis · Alcohol oxidation · Brookite TiO_2

1 Introduction

Photocatalytic reactions carried out by means of TiO_2 have been commonly applied to purification of waste waters and polluted air [1], and recently are finding industrial applications in several fields, such as in concrete materials or in surgery rooms, and yet in self-cleaning anti-fogging glass and textile applications [2]. Exploitation of photocatalysis in organic selective reactions has been achieved in organic solvents or in gas phase [3]. Very few examples of such reactions in aqueous environmentally friendly solvents have been reported [4]. Very recently our group has employed home prepared anatase and rutile TiO_2 samples to perform the partial oxidation of aromatic alcohols to aldehydes in water [5] by obtaining good conversions and selectivities. The selective oxidation of alcoholic group is a key step throughout many organic syntheses.

Here we report the 4-methoxybenzyl alcohol (MBA) partial oxidation carried out in water without any organic co-solvents in the presence of home-prepared pure brookite TiO_2. The formed aldehyde (*p*-anisaldehyde) is a species used in sweet blossom and flavour compositions for confectioneries and beverages and, furthermore, an intermediate in many different industrial processes.

The study was performed with two initial alcohol concentrations and three irradiation powers. The orthorhombic polymorph brookite TiO_2 has received less attention in the past, due to difficulties in synthesis to yield a single phase product. In recent years, however, new methods of brookite preparation have been developed [6] though not all have achieved pure brookite phase. Nanocrystalline TiO_2 sample, in which brookite is the predominant phase, was produced [6g] by a sol process under ambient condition and tested for methyl orange degradation in water where it showed a photocatalytic activity higher than that of Degussa P25 and rutile phase titania samples. Home-prepared brookite samples have been prepared here by following a calcination-free method recently optimised by our group [6i], starting from $TiCl_4$ aqueous HCl solutions, that implies the peptization with pure water of suspensions where pure particles of rutile and brookite are contemporary present. After decantation the surnatant of suspension, constituted of only brookite, was separated and dried.

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2 Experimental

The preparation and characterization of home prepared brookite has been elsewhere described [6i]. XRD patterns of the powders were recorded by using a Philips diffractometer using the CuKα radiation and a 2θ scan rate of 1.28° $\min^{-1}$. Raman measurements were carried out by a microprobe set-up (ISA-Jobin-Yvon, model Labram) equipped with a CCD detector and a He–Ne laser as excitation source (632.8 nm emission). A cylindrical Pyrex batch photoreactor with immersed lamp, containing 0.5 or 1.6 L of aqueous suspension, was used to perform the reactivity experiments. Initial alcohol concentrations were ca. 1 or 10 mM. 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. Medium pressure Hg lamps (Helios Italquartz, Italy) of powers equal to 125 (with 0.5 L reactor), 500 or 1,000 W (with 1.6 L reactor) were axially positioned within the photoreactor. The lamps were cooled by water circulating through a Pyrex thimble surrounding them; the temperature of the suspension was about 300 K. The radiation energy impinging on the suspension had average values of 10, 18 and 40 mW/cm^2 for the three powers, respectively. They were measured by using a radiometer UVX Digital, at 360 nm.

Before switching the lamp on, pure oxygen was bubbled into the suspension for 30 min at room temperature to reach the thermodynamic equilibrium. Adsorption of the alcohol 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 analyzed. NaOH 1 M solution was used to adjust the initial pH of the suspension to 7. All the used chemicals were purchased from Sigma-Aldrich with a purity >98%.

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 μm 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 5000A Shimadzu TOC analyser. BET specific surface areas were measured by the single-point BET method using a Micromeritics Flow Sorb 2300 apparatus.

3 Results and Discussion

The presence of brookite phase in the used samples was clearly showed by XRD diffraction and Raman spectroscopy. Figure 1 shows the XRD patterns of all the prepared samples. The main peak of brookite however overlaps with the main peak of anatase phase, so that it is not easy to discern between pure brookite and brookite-anatase mixtures. However Raman spectroscopy, performed on the pure brookite sample (Fig. 2), shows unequivocally the complete absence of anatase phase: in fact its characteristic peaks at 391^{-1} and 510 cm^{-1} are missing, whereas all the peaks attributable to brookite phase are well evident.

MBA was selectively oxidised mainly to 4-methoxybenzaldehyde (*p*-anisaldehyde, PAA) in a batch photoreactor under near-UV radiation. Two parallel reaction routes are present from the start of irradiation: partial oxidation to aldehyde and mineralization to CO_2.

The HPLC analyses, however, revealed the presence of small amounts of unidentified aromatic and aliphatic compounds. In this study alcohol initial concentrations of 1 and 10 mM have been used. The 10 mM concentration has been used to study the variation in selectivity and with up-scaling aims. It is worth noting that the maximum solubility of MBA in water is ca. 15 mM at room temperature. Table 1 reports the photoreactivity results obtained with home prepared catalyst, i.e. uncalcined brookite, brookite calcined at 723 K, mixture of rutile and brookite, rutile obtained after

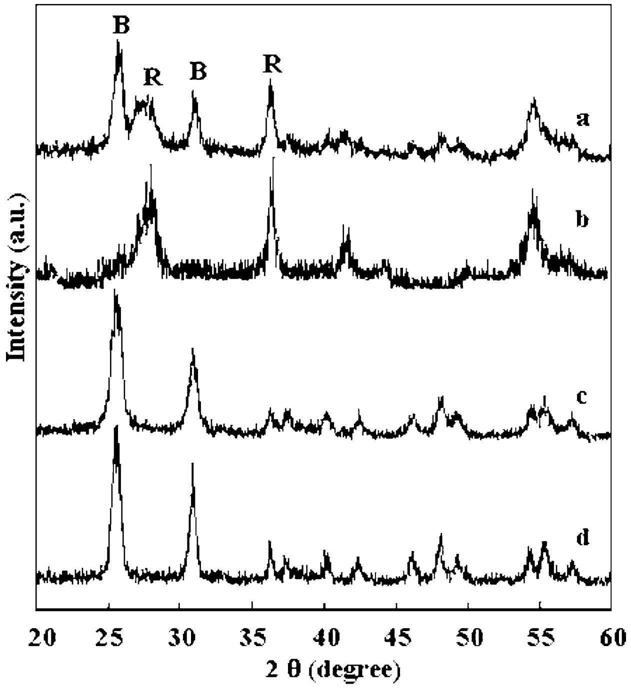

Fig. 1 XRD diffractogram of the samples: (**a**) brookite-rutile mixture; (**b**) pure rutile; (**c**) pure brookite; (**d**) calcined brookite. B = Brookite; R = Rutile

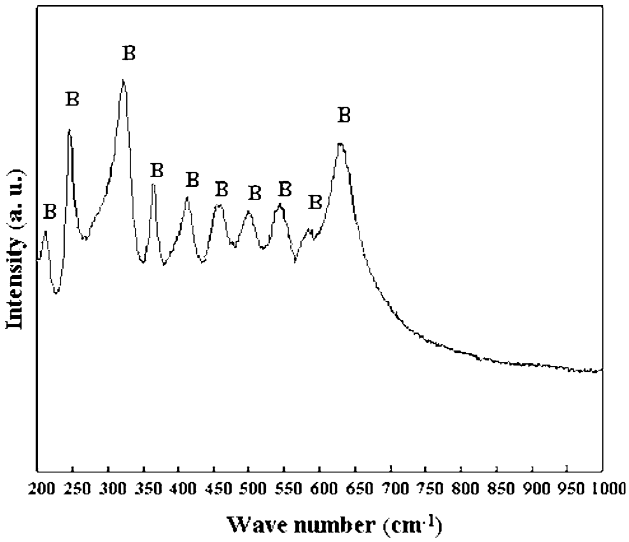

Fig. 2 Raman spectrum of a home-prepared pure brookite sample

separating the suspension during the preparation of samples. Results obtained with commercial TiO_2 samples are also reported for comparison purposes. In Table 1 the catalyst performance is quantified by the irradiation time for an MBA 50% conversion and the corresponding selectivity.

Preliminary runs indicated that no significant conversion of MBA occurs in the dark, both in the absence and in the presence of catalyst, even by continuously bubbling oxygen. Moreover MBA oxidation runs were carried out in irradiated aqueous solutions but in the absence of catalyst under experimental conditions similar to those used during the heterogeneous experiments. The reached conversions were found to be negligible (one order of magnitude lower than the photocatalytic ones) and a selectivity of ca. 41% was obtained. It was then assumed that the homogeneous oxidation process plays a negligible role in our heterogeneous systems.

Photocatalytic oxidation runs were carried out with brookite amounts in the 0.02–0.4 g/L range in order to determine the catalyst amount able to maximize the selectivity towards aldehyde (calculated as the ratio between the formed aldehyde and the converted alcohol). This study shows that the selectivities are indeed close each other independently of catalyst amount. Reaction rate values are quite different and significantly increase up to catalyst amounts of 0.4 g/L. Higher catalyst amounts have not been used because for 0.4 g/L almost all the photons were absorbed by the reacting suspension. The amount of transmitted photons has been estimated by measuring the irradiance at the outer wall of photoreactor. In Table 1 it may be seen that for catalyst amounts of 0.4 g/L the photon flow transmitted by the suspension represents always no more than 10–15% of the incident one (except for rutile). Consequently the catalyst amount used in all the MBA oxidation runs was 0.4 g/L.

The values of the specific surface areas (SSA) of the home-prepared samples are higher than those of the commercial ones tested, and a decrease can be observed only for Brookite 723 K and BrookiteRutile samples. This parameter was not considered important in this work as all the measurements were carried out at similar absorbed photons.

Uncalcined brookite used with a 10 mM MBA concentration gave rise to a good selectivity (52.5%) with reasonable reaction times (9.3 h). The reaction times for

Table 1 BET specific surface area (SSA) of catalysts and their performance in the photocatalytic oxidation of 4-methoxybenzyl alcohol to aldehyde

Catalyst	SSA (m^2/g)	Lamp irradiance (mw/cm^2)	Leaving irradiance (mW/cm^2)	MBA (mM)	Reactor volume (L)	Catalyst amount (g/L)	$t_{irr.}$ (h)	Selectivity (% mol)
Brookite	82	10	6.7	1	0.5	0.02	10.5	45
Brookite	82	10	4.0	1	0.5	0.1	2.7	45
Brookite	82	10	0.9	1	0.5	0.4	1.8	39
Brookite	82	10	0.9	10	0.5	0.4	9.3	52.5
Brookite	82	18	1.5	10	1.6	0.4	4.3	56
Brookite	82	40	3.0	10	1.6	0.4	3.6	48
Brookite 723 K	46	10	0.6	10	0.5	0.4	6.3	33
BrookiteRutile[a]	56	10	1.0	10	0.5	0.4	9.0	44
Rutile	24	10	3.7	10	0.5	0.4	12.5	31.5
Degussa P25[b]	50	10	0.10	1	0.5	0.4	0.7	8.3
Merck[c]	10	10	0.10	1	0.5	0.4	1.5	15.9
Sigma-Aldrich[d]	2.5	10	1.8	1	0.5	0.4	2.1	20.9

Irradiation time and selectivity have been calculated for 50% conversion

[a] % weight: 49.7 Brookite; 50.3 Rutile. [b] % weight: 80 Anatase; 20 Rutile. [c] Pure anatase. [d] Pure rutile

BrookiteRutile samples were slightly lower (9 h), showing a higher activity of this catalyst; however the selectivity was significantly higher by using pure brookite (52.5 vs. 44%). Moreover increasing the lamp power up to 500 W (17.5 mW/cm^2) surprisingly gave rise not only to higher reaction times, but also selectivities (56 vs. 52.5%). A further increase of lamp power to 1,000 W (40 mW/cm^2) resulted in a decrease of selectivity to 48%, probably due to the occurrence of severe oxidation leading to fast degradation of the formed aldehyde.

The excellent performance of brookite is of importance for future applications of this process where maximising times and selectivities can be reached by optimising light power. It is worth noting that this substrate amount allows for a production of ca. 0.7 g aldehyde (in 1.6 L reactor) in 5.3 h, by using 500 W lamp.

Figure 3 shows the trends of MBA, PAA and CO_2 concentrations, along with the C-balance, calculated as the sum of alcohol, aldehyde, and CO_2 concentrations. It can be seen that the uncalcined brookite is more selective than the calcined one. Moreover uncalcined brookite produces PAA and CO_2 in amounts that satisfy the C-balance up to 92% (Fig. 3a), the lacking carbon being justified by the production of small amounts of acid and hydroxylated aldehydes. In the case of calcined brookite the same C-balance fails of about 30% (Fig. 3b); the presence in the corresponding HPLC chromatograms of new unknown peaks at low retention times is a clear clue that aliphatic compounds are produced besides to acid and hydroxylated aldehydes.

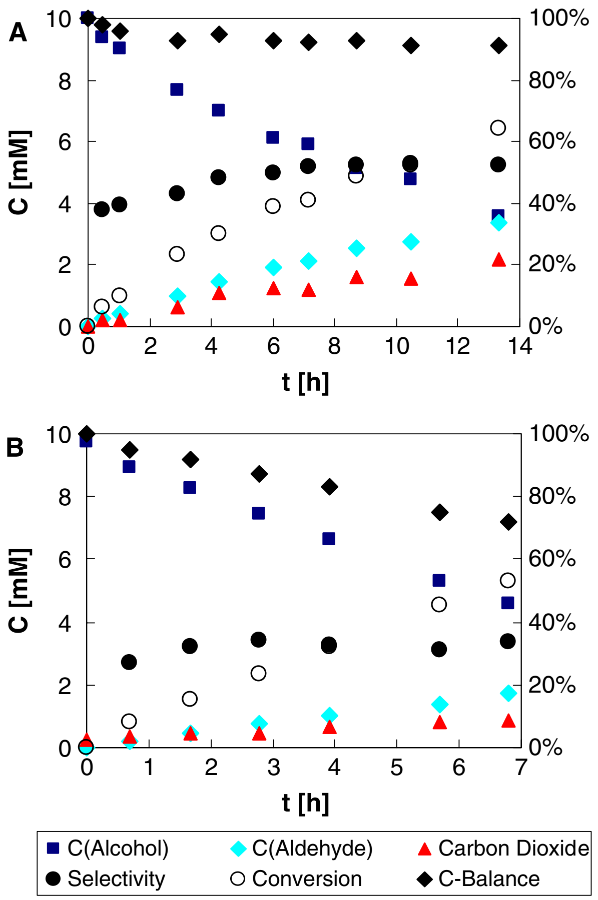

Fig. 3 Experimental results of a representative oxidation run of MBA with brookite TiO_2 uncalcined (**a**) and calcined at 723 K (**b**). Conversion and selectivity are scaled on right side. The CO_2 concentration values were divided by 8 for normalization purposes. Alcohol initial concentration: 10 mM; lamp irradiance: 10 mW/cm^2; catalyst amount: 0.4 g/L

The sample labeled as BrookiteRutile in Table 1 was prepared by directly drying the suspension obtained during the preparation, without applying the peptization method. The reaction rate was similar to uncalcined brookite, but selectivity was quite lower (44 vs. 52.5%). The separated rutile showed both lowest reactivity and selectivity among all the home-prepared catalysts. For commercial samples the data reported in Table 1 show that they are more reactive than brookite but the obtained selectivities are ca. 3 times lesser.

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