Visible-light-induced oxidation of *trans*-ferulic acid by TiO₂ photocatalysis

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A B S T R A C T

The oxidation of *trans*-ferulic acid ($C_{10}H_{10}O_4$) in aqueous TiO₂ dispersion occurs via the formation of a charge-transfer complex on the TiO₂ surface that is able to absorb visible light ($\lambda \geqslant 400$ nm). The main product is CO_2, whereas secondary oxidation products are organic species such as vanillin, caffeic acid, homovanillic acid, and vanillylmandelic acid. Oxidation through the formation of a charge-transfer complex occurs only in the presence of specific TiO₂ samples. Experiments in the absence of oxygen, in the presence of bromate ions and by using a phosphate-modified TiO₂, have been carried out for investigating the reaction mechanism. In order to study the interaction between *trans*-ferulic acid and TiO₂ surface and to characterize the charge-transfer complex, UV–Vis diffuse reflectance and FT-IR spectroscopies have been used. FT-IR characterization of TiO₂ samples in contact with the aqueous *trans*-ferulic acid solution indicates that the charge-transfer complex formation occurs via adsorption of bidentate ferulate species.

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1. Introduction

Among the advanced oxidation processes, photocatalysis in the presence of an irradiated semiconductor has proven to be very effective in the field of environmental remediation [1–6]. Despite the great research activity in the last two decades for obtaining a photocatalyst with optimal features, TiO₂ remains a benchmark against which any alternative photocatalyst must be compared. TiO₂ is indeed one of the most attractive photocatalytic materials due to its low cost, good chemical and photochemical stability, and nontoxicity. In general, pure TiO₂ with its large band gap (3.2 eV for anatase) can be activated only by near-UV light ($\lambda < 385$ nm), which represents a small fraction of solar light (about 3–4%). This inactivity under visible light strongly limits the practical application of TiO₂ photocatalyst. In order to overcome this drawback, pure TiO₂ has been modified by impurity doping and dye sensitization.

The doping has been done with ions of transitional metals, such as Co, Cr, Cu, Fe, Mn, Ni and V [7–10], and also of nonmetals such as B, C, N and S [11–14]. Recently, new visible responsive photocatalysts were prepared by modification of TiO₂ surface with noble metal complexes or nanoparticles. In particular, Au nanoparticles supported on TiO₂ have been successfully used for the oxidation of alcohols and for the reduction of nitrobenzene under visible irradiation [15]. The main drawback of these methods, however, is that the doping sites could act as recombination centers for the photoexcited electron–hole pairs. Consequently, sometimes the activity of these TiO₂-based photocatalysts does not improve.

In the dye sensitization, organic molecules coated on the TiO₂ surface are used to harvest incident light. Light absorption by the dye is followed by an electron injection from the excited state of the dye molecule into the conduction band of the semiconductor. The remaining positive hole is scavenged by a redox couple on the TiO₂ surface [16]. In the majority of dye-sensitized photoreactions, the dye molecule does not change its chemical nature in the course of the whole process. Another mechanism, called surface-complex charge-transfer mechanism, can be effective for the utilization of visible light. Dimitrijevic et al. [17] showed that the modification of TiO₂ nanoparticles with dopamine enables harvesting of visible light and promotes spatial separation of charges. Fullerol-modified TiO₂ exhibits visible-light photocatalytic activity [18]; in this case, the sensitization works through a single-step process, in which an electron is injected from a surface fullerol–TiO₂ complex to TiO₂ without involving the excited state of fullerol. This system is able to drive both photooxidative and photoreductive conversions, including the redox conversion of 4-chlorophenol, I⁻, and Cr(VI) and also the H₂ production. The degradation of salicylic acid under visible light [19] is ascribed to the formation of surface complexes of H_2O_2/TiO_2; the proposed reaction mechanism involves a photoinduced electron transfer of the surface complexes Ti–OOH. A complex between the TiO₂ surface and the

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nonionic surfactant having polyoxyethylene groups (Brij) exhibits visible-light activity for the reduction of CCl_4 and Cr(VI) [20]; the Brij/TiO_2 complex shows a broad absorption band in the 320–500 nm range. In the radical chain reaction of photosulfoxidation of alkanes, the starter radical is generated through absorption of visible light by the TiO_2–SO_2 complex [21]. Kim and Choi [22] investigated on the formation of surface complex between TiO_2 and EDTA, a common electron donor. The complex can absorb visible light through ligand-to-metal charge-transfer (LMCT) mechanism, and its activity is outstanding among all tested TiO_2–substrate complexes, giving rise to the photoreduction of Cr(VI) and production of H_2.

In some cases of dye-sensitized photoreactions, however, the same dye molecules change their chemical nature in the course of the whole process. Trichlorophenol in water forms a charge-transfer complex with TiO_2 that is activated by light wavelengths as long as 520 nm [23]. The trichlorophenoxyl radicals, resulting from charge-transfer, couple with each other to form a set of poly-aromatic chlorinated products, whose distribution is also affected by the light energy [24]. The degradation reaction of phenol, 2,4-dichlorophenol, and 4-chlorophenol in aqueous suspension of pure TiO_2 occurs under visible illumination ($\lambda > 420$ nm) by generating chlorides and CO_2 [25]. The surface complexation between phenolic compounds and TiO_2 appears to be responsible for the reactivity. The selective oxidation of benzyl alcohol to benzaldehyde under visible light in acetonitrile [26] proceeds through the formation of a characteristic complex of a benzyl alcoholic compound on the TiO_2 surface. The surface complexation mechanism is operative in the degradation of RS-2-(4-chloro-o-tolyloxy)propionic acid (mecoprop) on TiO_2 under visible light [27]. TiO_2 treated with mecoprop absorbs also in the visible region; the corresponding FTIR investigation showed that a charge-transfer complex between TiO_2 and mecoprop is formed through carboxylate formation.

This paper reports the results of a study in which trans-ferulic acid (FA, $C_{10}H_{10}O_4$, Fig. 1) is oxidized in aqueous TiO_2 dispersion irradiated by visible light. The oxidation process occurs through the formation of a charge-transfer complex able to absorb visible light ($\lambda \geqslant 400$ nm); it must be outlined that FA not only forms a complex on TiO_2 surface, but also itself undergoes the oxidation reactions. The photocatalytic oxidation of FA has been recently investigated under near-UV irradiation as a method both for water detoxification [28] and for chemical production of vanillin [29].

In this study, different commercial and home-prepared TiO_2 samples have been tested and a tentative mechanism to explain the occurrence of the photo-oxidation of FA up to CO_2 has been hypothesized. The interactions between FA and TiO_2 surface have been studied by means of UV–Vis diffuse reflectance and FT-IR spectroscopies.

2. Experimental

The photoreactivity experiments were performed by using two commercial TiO_2 samples, that is, Degussa P25 (ca. 80% anatase and 20% rutile, BET specific surface area, SSA, 50 $m^2\,g^{-1}$) and Merck (100% anatase, SSA: 10 $m^2\,g^{-1}$), and three home-prepared anatase TiO_2 samples (hereafter denoted as HPC3, HP1/50, and HP0.5). A P25 TiO_2 sample was modified by surface impregnation with phosphate ions. Also Al_2O_3 (Fluka type 507 C neutral, for
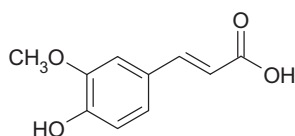

Fig. 1. Chemical structure of ferulic acid.

chromatography) and SiO_2 (silica gel for column chromatography, Riedel-de Haën) were used for blank experiments.

The amount of catalyst used for the runs was 0.6 $g\,L^{-1}$ for HPC3, HP1/50, and HP0.5, while it was 0.8 $g\,L^{-1}$ for Merck and 1 $g\,L^{-1}$ for the other powders. A systematic study on the dependence of the reactivity on the catalyst amount was performed only in the case of P25 TiO_2.

All the preparation details of HPC3, HP1/50, and HP0.5 samples are reported elsewhere [30–32]. In the following, only some essential information is reported. The HPC3 sample was prepared through a sol–gel route ex $TiCl_4$ (purity > 97%, Fluka) whose hydrolysis in water ($TiCl_4$/water = 1:11 v:v) produced a white sol that upon stirring for 10 h became a clear solution. Then, the suspension was dried and the sol was heated at 673 K for 3 h producing a powder with SSA of 35 $m^2\,g^{-1}$. For HP1/50 sample, the precursor solution was obtained by adding 20 mL of $TiCl_4$ to 1000 mL water contained in a volumetric flask; the addition was carried out very slowly without agitation in order to avoid the overheating of solution as the $TiCl_4$ hydrolysis is highly exothermic. At the end of the addition, the resulting solution was mixed for 2 min by a magnetic stirrer and then the flask was sealed and maintained at room temperature (ca. 298 K) for a total aging time ranging from 4 to 9 days. The sol became a transparent solution after ca. 12 h aging, and then, after waiting a few days, the precipitation process started. The colloidal dispersion was then dialyzed by using a dialysis tubing cellulose membrane (average flat width: 76 mm, Sigma Aldrich) until only a negligible amount of chloride ions was detected. The solid was then separated by centrifugation (20 min at 5000 rpm) and dried at room temperature by obtaining a powder with SSA of 118 $m^2\,g^{-1}$. For the HP0.5 sample, the precursor solution was obtained by slowly adding 5 mL of $TiCl_4$ drop wise into 50 mL of water in a beaker under magnetic stirring. After that, the beaker was closed and mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. This solution was boiled at 373 K for 0.5 h obtaining a white suspension that was then dried at 323 K in order to obtain the final solid consisting mainly of amorphous TiO_2 and crystals of anatase (75%) and rutile (25%). The powder was finally washed with distilled water and centrifuged several times until the chloride ion concentration in the washing water reached a negligible value.

Modification of P25 TiO_2 with phosphate was carried out as follows: 1 g of P25 TiO_2 and 2.76 g of NaH_2PO_4 (Sigma–Aldrich, >98% assay) were suspended in 50 mL water and mixed for 12 h. Then, the powder was recovered by centrifugation and suspended again in 50 mL of fresh NaH_2PO_4 solution. This operation was repeated two more times and then the powder was dried under vacuum at room temperature and finally ground.

Photocatalytic runs were performed by using a cylindrical batch photoreactor (CPR, internal diameter: 32 mm; height: 188 mm) of Pyrex glass. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases and for sampling. A 100 W 12 V halogen display/optic lamp (Osram GmbH, Germany) was axially positioned within the photoreactor. In order to cool the lamp and to cut off light emitted at $\lambda < 400$ nm (which was actually present in very small amount in the emission spectrum of the lamp), a 1 M aqueous solution of $NaNO_2$ (Sigma–Aldrich, >98% assay) was recirculated by means of a peristaltic pump through the Pyrex thimble surrounding the lamp. The radiation energy impinging on the suspension had an average value of 0.4 $W\,cm^{-2}$; it was measured between 450 and 950 nm by using a Delta Ohm 9721 radiometer. The aqueous suspension of TiO_2 (temperature of ca. 300 K; volume of 150 mL; catalyst amount: 0.6–3.0 $g\,L^{-1}$) was magnetically stirred, and air at atmospheric pressure was bubbled for 0.5 h before starting the runs and during the runs; the initial FA concentration was always 0.5 mM and initial pH ranged between 3.2 and 3.9. For a few runs, pure nitrogen was bubbled into the