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Photocatalytic degradation of formic and benzoic acids and hydrogen peroxide evolution in TiO_2 and ZnO water suspensions

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Abstract

The photocatalytic degradation of formic acid (FA) and benzoic acid (BA), chosen as model organic molecules with acidic properties, was investigated in TiO_2 and ZnO water suspensions under different experimental conditions. Hydrogen peroxide evolution, formed through a reductive pathway started by conduction band electrons, was also simultaneously monitored during the degradation runs. The effect of different initial amounts of substrates and the dependence of the reaction rate on the initial pH of the TiO_2 suspensions was interpreted under the light of a pseudo-steady state Langmuir–Hinshelwood rate form and of the electrostatic interactions occurring at the water–semiconductor interface. ZnO appeared a more effective photocatalyst than TiO_2 for BA, but not for FA degradation. A much higher amount of hydrogen peroxide was detected in ZnO irradiated suspensions, both in the presence and in the absence of the substrates, mainly because of its lower photocatalytic decomposition rate on such oxide. The rate of hydrogen peroxide evolution during the photocatalytic oxidation of BA on TiO_2 could be related to the rate of the oxidation process, while H_2O_2 could not be detected during the photocatalytic degradation of FA on this oxide, mainly because of the reduced shielding ability of this substrate.

Keywords: Photocatalytic degradation; Formic acid; Benzoic acid; Titanium dioxide; Zinc oxide; Hydrogen peroxide

1. Introduction

In recent years, many studies have been focused on the photocatalytic degradation of organic compounds mediated by semiconductor particles acting as photocatalysts [1–3]. In particular, titanium dioxide has been widely employed, thanks to its outstanding photocatalytic activity and high stability. Among other widely investigated semiconductors, zinc oxide also shows a high efficiency in photocatalysis, even if its low stability, which makes its aqueous suspensions stable only at basic pH, represents a strong limitation to its practical use [4,5]. The efficiency of photocatalytic processes has been shown to depend on several different characteristics of the semiconductor particles, such as their surface properties, the position of their band gap potentials, the mobility and recombination rate of the charge carriers generated by UV-light absorption. Moreover, a relevant role is also played by the chemical and adsorption properties of the degradation substrate, depending also on experimental conditions, such as pH and the substrate to photocatalyst concentration ratio.

The photocatalytic degradation of organic pollutants having direct relevance in water remediation treatments, i.e. 2-chlorophenol, a couple of acid azo dyes and the gasoline additive methyl *tert*-butyl ether, has been recently investigated by us [6–9]. In the present work, the interest was focused on the photocatalytic degradation of formic acid (FA) and benzoic acid (BA), two model compounds suitable for investigating the photocatalytic behaviour of aliphatic and aromatic organic acids, respectively. In particular, FA was chosen because it undergoes direct mineralisation to CO_2 and H_2O without the formation of any stable intermediate species [10–13]. Moreover, it also represents a possible final step in the photodegradation of more complex organic compounds. BA is a particularly suitable model molecule for understanding the photocatalytic behaviour of more complex aromatic water pollutants with acidic properties, initially undergoing hydroxylation of the benzene ring under photocatalytic conditions [14–16].

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The photocatalytic degradation of the two substrates was investigated in the presence of titanium dioxide and of zinc oxide under different experimental conditions. In particular, the effects of pH and of the initial substrate concentration were investigated in relation to the adsorption properties of the two substrates on the semiconductors. The evolution of hydrogen peroxide, formed by reduction of adsorbed molecular oxygen by conduction band electrons, was also monitored during the photodegradation runs; this gave information on the rate of the main reduction path occurring in parallel to the photocatalytic oxidative degradation of the two organic acids.

2. Experimental

2.1. Materials

Formic acid (purity 95–97%) and benzoic acid (purity >99.5%) were purchased from Aldrich. Titanium dioxide (Degussa P25, measured surface area 35 $m^2 g^{-1}$ [17]) and zinc oxide (Fluka, surface area 5 $m^2 g^{-1}$) were employed as photocatalysts. All other chemicals were high purity Aldrich products. Water purified by Milli-Q water system (Millipore) was used throughout.

2.2. Apparatus

All degradation runs were carried out at 35 ± 1 °C in a 400 mL cylindrical Pyrex closed reactor under magnetic stirring, by employing an experimental set-up similar to that already described [8,17]. Irradiation was performed by means of a 250 W iron alogenide lamp (Jelosil, model HG 200) emitting in the 315–400 nm wavelength range; its emission intensity on the reactor was 3.4×10^{-7} Einstein $s^{-1} cm^{-2}$, as periodically checked by ferrioxalate actinometry [18].

2.3. Procedure

Aqueous suspensions employed in photocatalytic runs usually contained 0.1 $g L^{-1}$ of TiO_2 or ZnO and a 5.0×10^{-4} M initial concentration of FA or a 1.0×10^{-4} M initial concentration of BA. The lamp was always switched on at least 30 min before the beginning of irradiation. All kinetic runs were performed under atmospheric conditions and constant magnetic stirring, as previously described [7,8]. Under so called natural pH conditions neither acids nor bases were added to TiO_2 suspensions, to avoid any possible interference of other species (mainly anions) on the photoredox reactions at the semiconductor–water interface. During the degradation runs under such conditions the pH increased, from an initial value of 3.5 to a final value of ca. 5.8 for FA and from 4.2 to ca. 6.0 for BA. On the contrary, when investigating the effects of different pH conditions, $HClO_4$ and NaOH or a 10^{-2} M NH_3/NH_4NO_3 buffer solution were added to adjust the pH of the suspensions. Both ClO_4^- and NO_3^- anions are expected to have negligible influence on the photocatalytic processes, because of their poor adsorption on the semiconductor surface and their low affinity for $^\bullet OH$ radicals [19]. When ZnO was employed as photocatalyst, the pH of the suspension was always maintained above 8.5, thus ensuring the photostability of the semiconductor oxide [20].

FA photodegradation was monitored by means of total organic carbon (TOC) analysis in the not purgeable organic carbon (NPOC) mode, employing a TOC-5000A Shimadzu instrument. BA concentration during the runs was detected by HPLC analysis, employing an Agilent 1100 Series apparatus, equipped with a μBondapak-C18 column and a UV–vis detector ($\lambda = 230$ nm). A water:methanol 72:28 mobile phase was used, flowing at 0.8 mL min^{-1}. Absorption spectra were successively recorded during BA photodegradation ($\lambda_{max} = 225$ nm) by means of a Perkin-Elmer Lambda 16 apparatus [8] and the extent of mineralisation was also determined by TOC analysis. The photocatalyst particles were removed by centrifugation at 3000 rpm for 30 min prior to any analytical determination on the samples (2 mL) periodically withdrawn from the irradiated suspensions. All runs were repeated at least twice to check their reproducibility.

The hydrogen peroxide concentration was monitored during the photodegradation runs by a fluorimetric analysis ($\lambda_{ex} = 316.5$ nm, $\lambda_{em} = 408.5$ nm) of the fluorescent dimer formed in the horseradish peroxidase catalysed reaction of H_2O_2 with *p*-hydroxyphenylacetic acid [21,22], using a 650-10S Perkin-Elmer fluorescence spectrophotometer. Hydrogen peroxide standard solutions employed in calibration were analysed iodometrically.

Adsorption tests of the two acids were performed in aqueous suspensions containing 1.0 $g L^{-1}$ of TiO_2 at different pH or 1.0 $g L^{-1}$ of ZnO at basic pH, which had been maintained in the dark under constant stirring at 35 °C for 24 h. The fraction of FA and BA adsorbed on the photocatalyst was determined by TOC and spectrophotometric analysis, respectively, after removal of the powder by filtration through Millipore 0.22 μm disks and by centrifugation.

3. Results and discussion

3.1. Adsorption equilibria involving FA and BA

Preliminary studies of FA and BA adsorption on titanium dioxide and zinc oxide were performed in suspensions containing a standard initial concentration of the two acids and an amount of the two oxides which was 10-fold higher than that employed in the photocatalytic runs. The extent of FA adsorption on the surface of both oxides was always found to be negligible, in agreement with previous data [23,24]. Very recent FA adsorption measurements, performed in the presence of a higher amount of TiO_2 P25 than that of the present study [24], predict in fact a less than 0.05 ppm concentration decrease in the aqueous phase due to FA adsorption under our conditions, which of course would be undetectable.

On the contrary, BA adsorption was not negligible on 1.0 $g L^{-1}$ of titanium dioxide. As shown in Table 1, maximum adsorption occurred under natural pH conditions, while the BA adsorbed fraction was lower at lower pH and no adsorption could be detected on both TiO_2 and ZnO at basic pH. The observed trend clearly reflects the electrostatic interactions at the