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Photocatalytic degradation of organic compounds in aqueous systems by transition metal doped polycrystalline TiO_2

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Abstract

Some probe catalytic photooxidation reactions with aliphatic and aromatic organic compounds having different acid strengths, i.e. methanoic acid, ethanoic acid, benzoic acid and 4-nitrophenol, were carried out in aqueous systems by using polycrystalline TiO_2 powders doped with various transition metal ions (Co, Cr, Cu, Fe, Mo, V and W). The Co-doped powder showed to be more photoactive than the bare TiO_2 for methanoic acid degradation while the behaviour of TiO_2/Cu and TiO_2/Fe was similar to that of the support. TiO_2/W was the most efficient sample for the photodegradation of benzoic acid and 4-nitrophenol, TiO_2 the most active powder for ethanoic acid. A tentative explanation is provided by taking into account: (i) the dissociation constants (K_a) of the different acids used as substrates; (ii) their aliphatic or aromatic nature; (iii) the points of zero charge (PZC) of the photocatalysts; (iv) their relative rate constants for photoelectron–hole recombination (k_r) determined by femtosecond pump-probe diffuse reflectance spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

TiO_2 is widely used as photocatalyst because of its optical and electronic properties, low cost, chemical stability and non-toxicity [1–3]. Due to its band-gap energy, TiO_2 utilizes only a very small fraction of the solar spectrum and thus doping with transition metals has been employed to extend the light absorption to the visible region [4–15]. The presence of foreign metal species is generally detrimental for the degradation of organic species in aqueous systems but many controversial results are reported. Cr^{3+} normally reduces the photocatalytic performances of TiO_2 [5] but Cr and V ion implanted TiO_2 have showed photocatalytic reactivity higher than TiO_2 for the decomposition of NO under solar beam irradiation [16]. Choi et al. [8] found that doping quantum-sized TiO_2 with Fe^{3+}, Mo^{5+}, Ru^{3+}, Os^{3+}, Re^{5+}, V^{4+} and Rh^{3+} enhances the photoreactivity both for the oxidation of $CHCl_3$ and the reduction of CCl_4, while doping with Co^{3+} and Al^{3+} decreases the photoactivity. The photocatalytic efficiency of TiO_2 toward the oxidation of 1,4-dichlorobenzene is improved by the introduction of WO_3 and MoO_3 [10,11] and a beneficial influence of tungsten was found for the photodegradation of 4-nitrophenol [12,13].

A comparison among the results reported in the literature for doped samples obtained from various preparations is not easy because the experimental conditions under which the runs were carried out and the preparation methods of the samples are usually

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different. Moreover, the photoactivity cannot be generally straightforwardly related only to few properties because it depends on all of them. In order to compare the photoactivity of variously doped TiO_2 samples, it would be necessary to use the same bare TiO_2 as starting material by scrutinising carefully the various findings deriving from the characterisation results and to evaluate their relative importance.

In this paper the preparation of TiO_2 polycrystalline powders doped with some transition metal ions is reported. The samples have been characterised by X-ray diffractometry, specific surface area (SSA) determinations, measurements of the points of zero charge (PZC) and femtosecond pump-probe diffuse reflectance spectroscopy. A correlation of the acid–base properties of the powders and/or the relative recombination rate of the photoexcited electrons and holes with the photocatalytic activity is reported for the photooxidation in aqueous systems of some probe aliphatic and aromatic organic molecules with different acid strengths, i.e. methanoic acid ($K_a = 1.77\times10^{-4}$, 293 K), ethanoic acid ($K_a = 1.76\times10^{-5}$, 298 K), benzoic acid ($K_a = 6.46\times10^{-5}$, 298 K), and 4-nitrophenol ($K_a = 7.00\times10^{-8}$, 298 K).

2. Experimental

2.1. Sample preparation

The doped samples were prepared by the incipient wet impregnation method. Bare TiO_2 was obtained by reacting an aqueous solution of $TiCl_3$ with ammonia. The solid was filtered, washed repeatedly to remove residual Cl^- ions and finally heated in air for 24 h at 773 K. The TiO_2 support was impregnated with aqueous solutions of transition metal ions ex $Co(NO_3)_2\cdot6H_2O$, $Cr(NO_3)_3\cdot9H_2O$, $Cu(NO_3)_2\cdot3H_2O$, $Fe(NO_3)_3\cdot9H_2O$, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, NH_4VO_3 and $(NH_4)_6W_{12}O_{39}\cdot xH_2O$. Water was evaporated by heating the samples at 373 K for 24 h. The amounts of support and solution were chosen to yield solids containing 1.0 mol of dopant metal ions over 100 mol of dopant and titanium ions. The dried solids were manually ground in an agate mortar and calcined in air at 773 K for 24 h.

The samples were identified by the following code: TiO_2/Me, where Me indicates the kind of dopant metal ion. A detailed characterisation of similar samples is reported elsewhere [17].

2.2. X-ray Diffraction (XRD)

The XRD patterns of the powders were collected by a Philips powder diffractometer using the Cu Kα radiation.

2.3. SSA determination

The SSAs were measured by the single-point BET method using a Flow Sorb 2300 apparatus (Micromeritics International Corp.).

2.4. PZC determination

The PZC of the various powders was estimated by using the method of mass titration [18] which involves finding the limiting pH value of an oxide/water slurry as the oxide mass content is increased. Varying amounts of powders were added to water and the resulting pH values were measured after 24 h of equilibration [17].

2.5. Femtosecond pump-probe diffuse reflection spectroscopy

The relative rate constants of electron–hole recombination were estimated by using the femtosecond pump-probe diffuse reflectance spectroscopy technique whose details are described elsewhere [19].

2.6. Photocatalytic experiments

The photoreactivity experiments were carried out in a cylindrical Pyrex glass reactor containing 700 mg of catalyst and 500 ml of aqueous solutions of methanoic acid, ethanoic acid, benzoic acid or 4-nitrophenol. The amount of organic compound was 20 mg L^{-1}, corresponding to a concentration ranging from 4.35×10^{-4} to 1.44×10^{-4} M, depending on the substrate. A 125 W medium pressure Hg lamp (Helios Italquartz) immersed within the photoreactor was used and the mean value of the incident radiation power, determined using an UV radiometer (Digital, UVX 36), was 13.5 mW cm^2. Oxygen was continuously bubbled into the stirred suspension.

Samples of 5 ml volume were withdrawn at fixed intervals and, after filtration, the concentration of the substrates was determined. The analysis of 4-nitrophenol was performed by measuring its absorption at 315 nm by means of an UV-2401 PC Shimadzu spectrophotometer. The concentrations of ethanoic acid and benzoic acid were evaluated by using an HPLC Varian 9010 Solvent Delivery System coupled with a Varian 9050 Variable Wavelength UV–Vis Detector. The column was a Varian Chromsep C18 5 μm (150 mm long × 4.6 mm i.d.). The eluent for ethanoic acid was a 50 mM $NH_4H_2PO_4$ aqueous solution (pH = 3) and CH_3CN (95/5, v/v) with a flow rate of 1 ml min^{-1}, while for benzoic acid a 50 mM KH_2PO_4 aqueous solution (pH = 3.8) and CH_3OH (55/45, v/v) with a flow rate of 2 ml min^{-1} was used. For methanoic acid only total organic carbon (TOC) determinations were carried out by using a TOC-5000A Shimadzu Total Organic Carbon analyser. The moles of methanoic acid were calculated from the TOC values. For the other substrates TOC analyses were performed in addition to the HPLC ones.

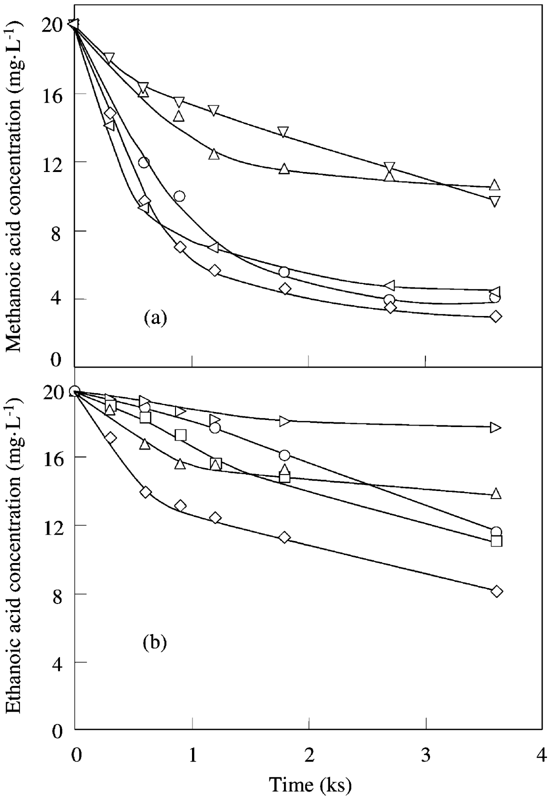

Fig. 1. Photooxidation of aliphatic substrates on bare and transition metal-loaded TiO_2 powders: (a) methanoic acid; (b) ethanoic acid. (◇) TiO_2; (◁) TiO_2/Co; (△) TiO_2/Cr; (○) TiO_2/Cu; (▽) TiO_2/Mo; (▷)TiO_2/V; (□) TiO_2/W.

3. Results and discussion

The XRD patterns of the various samples showed that all the powders consisted mainly of a mixture of anatase and rutile in the ratio of ca. 4:1 [17].

The apparent kinetics of disappearance of the four organic compounds was followed by determining the concentration of the substrates at various time intervals. Figs. 1 and 2 show results of the photoreactivity experiments obtained in the presence of representative samples. The time required for the complete phototransformation of the substrates depended both on the compound and on the employed sample. The addition of transition metal ions to polycrystalline TiO_2 was generally detrimental with the exception of some metals and particular substrates.

Table 1 reports the initial reaction rates per square meter of photocatalyst (r'_0), the relative rate constants of recombination of the photoexcited electrons and holes (k_r), the PZC and the BET SSAs of the various samples.

In a semiconductor photocatalyst, band-gap photoabsorption generates electrons and holes which can migrate to the surface to drive redox reactions with adsorbed substrates, competing with their disappearance due to mutual recombination. Certain surface sites can trap the photoexcited electrons before their recombination with the holes. The lifetime of trapped electrons has been related to the photocatalytic activity of bare and metal-loaded TiO_2 powders [19,20]. As a general trend, the lower the electron–hole recombination rate, the higher the photocatalytic activity of the samples. Table 1 shows that the k_r values of the loaded samples are always higher than that of the support, indicating that loading enhances the e^-–h^+ recombination.

The PZC of an oxide is the value of pH required to give zero net surface charge [21]. The knowledge of the PZC helps to predict whether there occurs preferentially the ion exchange to a specific component of the oxide system, influencing so the photoreactivity of the powder. As shown in a previous paper [17], the

PZC of transition metal-loaded TiO_2 powders depends both on the type and amount of dopant metal. The results of Table 1 reveal that TiO_2/Cr presents the lowest value of PZC followed by TiO_2/V and TiO_2/Mo. The PZCs of the other loaded samples are quite similar to that of bare TiO_2.

Fig. 1a shows that loading TiO_2 with Co, and Cu scarcely influences the photocatalytic activity of the pure support for methanoic acid degradation. The initial reaction rate of TiO_2/Co is higher than that of TiO_2 while the r'_0 values of TiO_2/Cu and TiO_2/Fe (see Table 1) are similar to that of the support. The powders doped with Cr and Mo revealed a not significant photoactivity. As far as ethanoic acid is concerned (Fig. 1b), TiO_2 is the most photoactive sample and no significant differences were noticed in the behaviour of the various loaded samples with the exception of TiO_2/V which showed a low value of r'_0.

For the degradation of benzoic acid and 4-nitrophenol (Fig. 2) the most efficient samples were TiO_2/W and TiO_2. The trends of the initial reaction rates were substantially the same for the two aromatic substrates with the exception of TiO_2/Cu and TiO_2/Co for which an inversion of the values was observed.

A tentative explanation of the observed photoreactivity can be provided by taking into account the nature of the reacting molecules and the acid–base and electronic properties of the photocatalysts. Concerning metanoic acid degradation, the photoreactivity of the samples doped with Co, Cu and Fe is higher or similar to that of TiO_2. This can be attributed to the relatively basic PZC values of these powders since HCOOH is more acidic compared with the other substrates, and then a stronger interaction with a quite

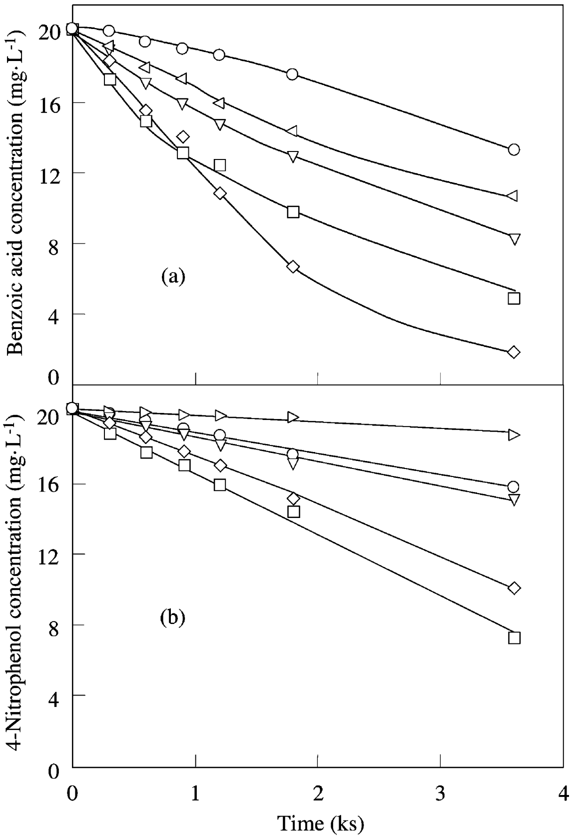

Fig. 2. Photooxidation of aromatic substrates on bare and transition metal-loaded TiO_2 powders: (a) benzoic acid; (b) 4-nitrophenol. (◇) TiO_2; (◁) TiO_2/Co; (○) TiO_2/Cu; (▽) TiO_2/Mo; (▷) TiO_2/V; (□) TiO_2/W.

Table 1
SSA, PZC, relative rate constants for photoelectron–hole recombination (k_r) and initial photooxidation rates (r'_0) of the various samples

Catalyst	SSA ($m^2\,g^{-1}$)	PZC (pH)	k_r ($cm^3\,ps^{-1}$)	$r'_0 \times 10^{10}$ ($mol\,L^{-1}\,s^{-1}\,m^{-2}$)			
				Methanoic acid	Ethanoic acid	Benzoic acid	4-Nitrophenol
TiO_2	55	7.1	1.4	83.0	60.2	14.7	4.4
TiO_2/Co	49	7.7	2.5	102.4	20.1	9.5	2.3
TiO_2/Cr	50	3.3	2.3	34.6	25.2	2.4	1.2
TiO_2/Cu	43	7.6	2.3	76.1	11.2	4.2	3.1
TiO_2/Fe	50	7.4	4.1	75.4	15.2	3.8	2.0
TiO_2/Mo	49	5.8	2.1	29.6	23.2	11.9	3.9
TiO_2/V	43	5.4	3.1	52.1	8.3	2.2	1.1
TiO_2/W	55	6.6	1.9	60.0	17.7	18.2	6.4

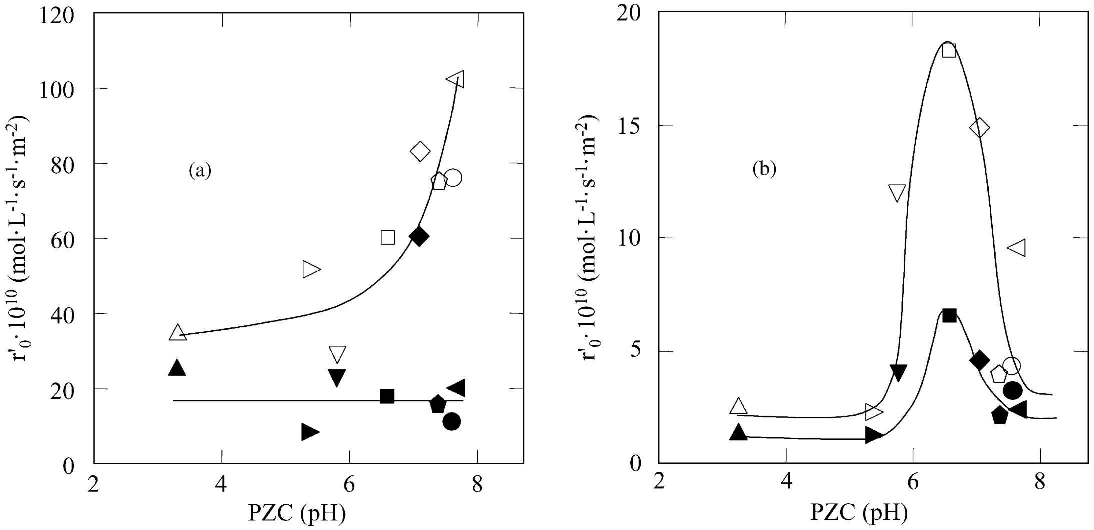

Fig. 3. Plot of r'_0 versus PZC values: (a) open symbols: methanoic acid; filled symbols: ethanoic acid. (b) open symbols: benzoic acid; filled symbols: 4-nitrophenol. (◇) TiO_2; (◁) TiO_2/Co; (△) TiO_2/Cr; (○) TiO_2/Cu; (⬠) TiO_2/Fe; (▽) TiO_2/Mo; (▷) TiO_2/V; (□) TiO_2/W.

basic catalyst surface probably occurs. It is worth noting that TiO_2/Fe exhibits practically the same r'_0 of the most active samples although its high k_r value would suggest the occurrence of a low photocatalytic activity. Therefore the values of PZC appear to address the photoreactivity of the samples and this seems confirmed by the observation of Fig. 3a which shows a plot of r'_0 as a function of the PZC values of the samples. Indeed, the enhancement of the degradation rate seems related with the increase of PZC.

To relate the dissociation constants of the acids with their interaction with the catalyst surface is obviously

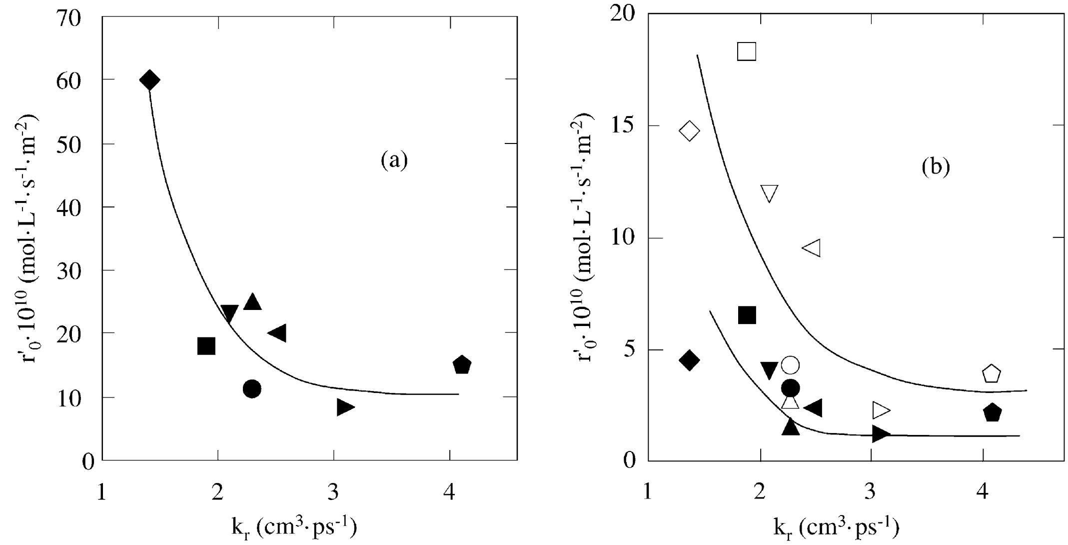

Fig. 4. Plot of r'_0 versus k_r values: (a) ethanoic acid; (b) open symbols: benzoic acid; filled symbols: 4-nitrophenol. The meaning of the symbols are same as those of Fig. 3.

a rough approximation because their values are in principle valid only for bulk liquids. Indeed, the formation of the double layer at the liquid–solid interface could influence both the dissociation and the polarisability of the reacting molecules. Unfortunately it is not easy a thorough investigation of these phenomena under the experimental conditions employed in this study.

In Fig. 3a the r'_0 values of ethanoic acid photodegradation are also reported. In this case a straightforward relation with the PZCs cannot be noticed (the reaction rate appears to be almost independent of PZC), probably because this substrate is less acidic than HCOOH (K_a is approximately an order of magnitude smaller). On the other hand, as shown in Fig. 4a, the relation between rate of ethanoic acid degradation and k_r does not help to address the photoreactivity. Indeed, for $k_r > 1.9\,\mathrm{cm^3\,ps^{-1}}$ the reaction rate becomes independent of k_r probably because the recombination of the photogenerated pairs is too fast. The net activity could depend on the electron–hole recombination rate only when the k_r values are relatively low as in the case of bare TiO_2.

The data of r'_0 versus k_r for methanoic acid have not been reported in Fig. 4a because they are randomly scattered, indicating that k_r is not a significant parameter for the photooxidation of this small molecule.

As far as the degradation of both aromatic substrates is concerned, Fig. 3b reveals a maximum of photoreactivity for TiO_2/W whose PZC = 6.6 is not too acid and k_r value is the lowest among the loaded samples, not very different from that of TiO_2. Instead, the photoactivity of all the other loaded samples is lower than that of the pure support. The beneficial effect due to the presence of tungsten has been reported previously for many molecules [10–12,17], including 4-nitrophenol, and it has been explained by considering the formation of W(V) species by means of a transfer of photogenerated electrons from TiO_2 to W(VI). Subsequently W(V) could be oxidised to W(VI) by transferring electrons to adsorbed O_2.

Fig. 4b shows that the correlations between rates of photooxidation and k_r values of the various samples are similar both for benzoic acid and 4-nitrophenol indicating that the aromatic nature of the two molecules prevails on the remarkable differences of acidity (K_a of C_6H_5COOH is three order of magnitude higher than K_a of 4-nitrophenol). It is worth noting that also for the degradation of these substrates the k_r values become the dominant factor only when the recombination of the photogenerated pairs is not too fast. By taking into account that the molar concentration of benzoic acid and 4-nitrophenol is not much different from that of the two aliphatic compounds, the low r'_0 values found for the degradation of the aromatic substrates can be understood by considering a likely steric effect of these big molecules. It can be hypothesised that a smaller number of adsorbed molecules is necessary to form a monolayer and consequently those transformed by means of a primary oxidant attack (it should be reminded that r'_0 is related to the initial reaction rate) are less numerous.

TOC results indicate that the mineralization of all the substrates is achieved more quickly in the presence of bare TiO_2. Very surprisingly, as shown by Fig. 5, the aliphatic acids are mineralized after times longer than those of the aromatic compounds even if

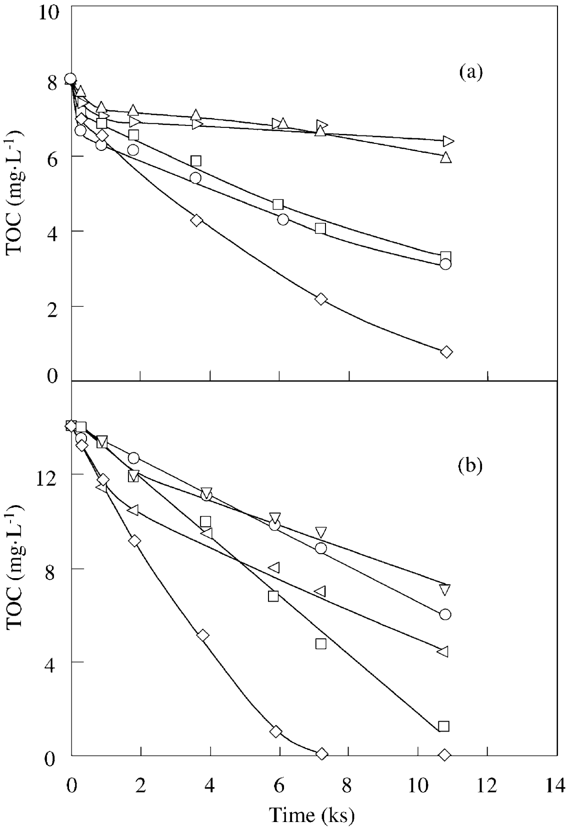

Fig. 5. TOC degradation of different substrates: (a) ethanoic acid; (b) benzoic acid. The meaning of the symbols are the same as those of Fig. 3.

the number of atoms of carbon is smaller. The occurrence of strong acid–base interactions between the surface Lewis acid sites and methanoate or ethanoate chelating species, could partially deactivate the photocatalysts. This phenomenon, whose extent depends on the different surface acidity of the powders, could be responsible also for the decrease in the time of the reaction rate of substrate disappearance (see Fig. 1a and b).

As already found in previous works [17,22], the initial rate of mineralization of ethanoic acid in the presence of TiO_2/Cu (Fig. 5a) is the highest one. Nevertheless, the corresponding r_0' value found with this sample is very low (Fig. 1b and Table 1) and this finding can be interpreted by hypothesising that, differently from the other powders, initially the presence of copper species onto TiO_2 surface favours the mineralization of ethanoic acid without formation of persistent intermediates.

For benzoic acid and 4-nitrophenol a weaker interaction likely occurs caused by the electrons of the aromatic ring rather than the carboxylic and OH groups.

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