

Transition metal doped TiO₂: physical properties and photocatalytic behaviour

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ABSTRACT. Two probe photocatalytic reactions, i.e. ethanoic acid and 4-nitrophenol photooxidation, were carried out in different experimental conditions by using suspensions of transition metal (Co, Cr, Cu, Fe, Mo, V and W) doped polycrystalline TiO₂ powders in aqueous systems. A beneficial influence of the presence of metal species was observed only with the samples containing copper and tungsten. In particular, the TiO₂/Cu powders showed to be more photoactive of bare TiO₂ for the ethanoic acid oxidation while the TiO₂/W samples were more efficient for 4-nitrophenol degradation. A tentative interpretation is provided on the basis of the values of the points of zero charge of the powders and of the rate constants of recombination of photogenerated electrons and holes, determined by femtosecond pump-probe diffuse reflectance spectroscopy (PP-DRS).

1. INTRODUCTION

TiO₂ is a very suitable photocatalyst because of its optical and electronic properties, low cost, chemical stability and non-toxicity [1-3]. However, due to its bandgap energy, TiO₂ utilizes only a very small fraction of the solar spectrum and thus doping with transition metals has been so far 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 but many controversial results are reported in literature. Hoffmann *et al.* [8] found that doping quantum-sized TiO₂ with Fe³⁺, Mo⁵⁺, Ru³⁺, Os³⁺, Re⁵⁺, V⁴⁺ and Rh³⁺ at 0.1-0.5 at. % significantly enhanced the photoreactivity both for the oxidation of CHCl₃ and the reduction of CCl₄, while Co³⁺ and Al³⁺ decreased the photoreactivity. The photocatalytic activity of TiO₂ toward the oxidation of 1-4 dichlorobenzene was improved significantly by the introduction of WO₃ and MoO₃ [10, 11] and a beneficial influence of tungsten was found for the photodegradation of 4-nitrophenol [12, 13]. Cr³⁺ is reported to reduce significantly the photocatalytic performances of TiO₂ [5] but Cr and V ion implanted TiO₂ have showed photocatalytic reactivity three and four times higher than TiO₂ for the decomposition of NO under solar beam irradiation [16]. The method of doping obviously determines the properties of the catalyst, so that direct comparisons on the effects of metal doping require identical experimental conditions for the preparation of the samples and the use of the same bare TiO₂ as starting material.

The photoreactivity of the catalysts depends on several factors as for example the acid-base properties of the powders and/or the relative recombination rate of the photoexcited electrons and holes. In this work we

have tried to correlate these physical properties with the photocatalytic behaviour of polycrystalline TiO₂ powders doped with some transition metals. The activity of the samples was tested in different photocatalytic reaction systems.

2. MATERIALS AND METHODS

2.1. Sample preparation. The doped samples were prepared by the incipient wet impregnation method. The TiO₂ support was obtained as follows: titanium hydroxide was precipitated by reacting an aqueous solution of TiCl₃ with ammonia, the white precipitate was washed repeatedly to remove residual Cl⁻ ions, dried 24 h at 373 K and finally heated in air for 24 h at 773 K. TiO₂ was impregnated with aqueous solutions of transition metal ions ex Co(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, Fe(NO₃)₃·9H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, NH₄VO₃ and (NH₄)₆W₁₂O₃₉·xH₂O. After standing at room temperature for 24 h, 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 0.3, 1.0, 2.0 and 5.0 moles of dopant metal ions over 100 moles 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: TiO₂/Me/X, where Me indicates the kind of dopant metal ion and X its molar percentage.

The detailed characterization of these samples by means of X-ray diffraction, specific surface area measurements and scanning electron microscopy, will be published elsewhere [17].

2.2. Point of zero charge determination. The point of zero charge of the various powders was esti-

mated 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. Typical values of oxide/water by weight were 0.1, 1, 5, 10 and 20%.

2.3. 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 (PP-DRS) technique whose details are described elsewhere [19].

2.4. Photocatalytic experiments. The samples were employed as catalysts for two different photocatalytic reactions: (a) oxidation of ethanoic acid and (b) photodegradation of 4-nitrophenol.

(a) 50 mg of photocatalyst were suspended with magnetic stirring in 5 ml of an aqueous solution of ethanoic acid (5 vol. %) and photoirradiated in air. Irradiation with light of wavelength $\lambda > 300$ nm was carried out using a 400 W high pressure Hg arc (Eiksha) through a cylindrical Pyrex glass filter and a closed glass reaction tube. Carbon dioxide was analyzed by gas chromatography.

(b) The experiments were performed by using a cylindrical Pyrex glass reactor containing 700 mg of catalyst and 500 ml of an aqueous solution of 4-nitrophenol ($20 \text{ mg} \cdot \text{L}^{-1}$) previously adjusted to pH 4.5. Oxygen was continuously bubbled into the stirred suspension which was irradiated by a 125 W medium pressure Hg lamp (Helios Italquartz) immersed within the photoreactor. Samples of 5 ml volume were withdrawn from the suspension at fixed intervals and, after filtration, the concentration of 4-nitrophenol was evaluated by measuring its absorption at 315 nm with a spectrophotometer Beckman DU 640.

3. RESULTS AND DISCUSSION

3.1. pzc measurements. The pH of an aqueous suspension of an oxide depends on the amount of powder in a given volume of water [20–22]. The point of zero charge of the oxide is the value of pH required to give zero net surface charge. The adsorption sites for anions and cations are charged surface groups resulting from the protonation-deprotonation equilibria of the surface hydroxy groups of the oxide. The knowledge of the pzc can help, in principle, to predict whether the ion exchange to a specific component of the oxide system is or not favoured.

The pzc of a composite oxide is related to the values of the pure oxide components and has values that lie between those of the two phases [23, 24]. As found by Subramanian *et al.* [23] the surface charge devel-

opment of a supported oxide is a function of dopant concentration.

According to Noh and Schwarz [18], the observation of a limiting pH value as one increases the mass fraction of solid in fresh water can be considered as an estimation of the point of zero charge of pure and composite oxides. Figure 1 shows typical plots of pH versus mass percentage of oxide for bare TiO_2 and the powders doped with W. The plateaus of the mass titration curves are the pH values corresponding to the pzc's of the samples. Similar curves were obtained for all the doped samples.

A decrease in pH is observed when the pH_{pzc} is lower than 7 since the surface sites tend to become negatively charged either by adsorbing OH^- ions or by desorbing H^+ ions. On the contrary, an increase in pH occurs if the pH_{pzc} is higher than 7 since in this case the solid surface will be positively charged.

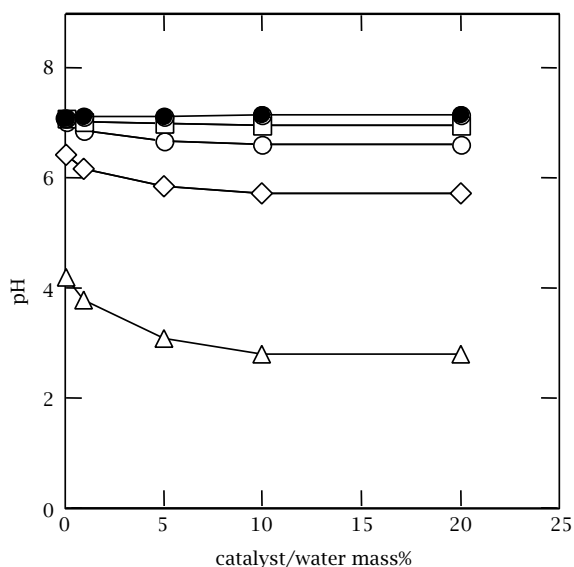


Figure 1. (a) Plot of pH versus the catalyst/water mass percentage for TiO_2 and various TiO_2/W samples: (●) TiO_2 , (□) $\text{TiO}_2/\text{W}/0.3$, (○) $\text{TiO}_2/\text{W}/1.0$, (◇) $\text{TiO}_2/\text{W}/2.0$, (△) $\text{TiO}_2/\text{W}/5.0$.

The pzc values have been plotted against the content of dopant. As shown in Figure 2, the pzc of Cr, Mo, V and W-doped TiO_2 moves to a lower pH as the content of metal increases, whilst for Co, Cu and Fe-doped TiO_2 , the pzc moves to a value more basic than that of the bare TiO_2 . The points of zero charge of the various powders are also reported in Table 1.

The pzc's of the samples containing Mo, V and W significantly decrease with increasing the metal content indicating a surface enrichment of species with an acid behaviour as MoO_3 , V_2O_5 or WO_3 . For the Cr-doped samples, 0.3 at. % of metal is sufficient to modify strongly the pzc of TiO_2 from 7.1 to 3.6 suggesting the

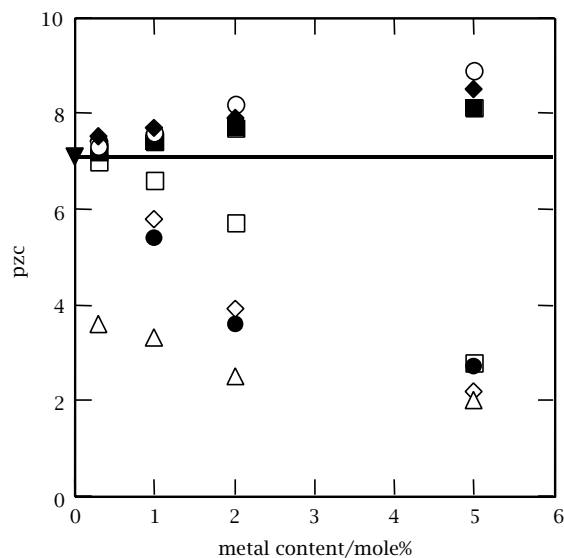


Figure 2. (b) Points of zero charge of the doped samples versus the amount of metal content (%): (▼) TiO₂, (◆) TiO₂/Co, (△) TiO₂/Cr, (○) TiO₂/Cu, (■) TiO₂/Fe, (◇) TiO₂/Mo, (●) TiO₂/V, (□) TiO₂/W.

presence of CrO₃ on the surface of the support, as already found in previous studies [25].

3.2. Femtosecond pump-probe diffuse reflectance spectroscopy. Femtosecond (PP-DRS) measurements were carried out on bare and metal doped TiO₂ powders to obtain the rate constants of recombination of photoexcited electrons and holes.

A pump beam of wavelength at 310 nm induces a very rapid (< ca. 250 fs) rise of absorption at 620 nm followed by a gradual decay [26]. The rapid rise is thought to be due to the capture of photoexcited electrons at a trapping site and their recombination with holes induces the decay of the absorption in the time region of several hundreds ps. The decay profiles can be simulated on the assumption of a second order kinetics of electron-hole recombination [19].

All the undoped and doped TiO₂ powders showed similar decay profiles and by analyzing the decay curves of the various samples it was possible to estimate the rate constants of charge recombination, k_r (cm³ ps⁻¹), which are listed in Table 1. The k_r values of some samples containing 5% of metal are not reported because the measurements were not accurate and reproducible due to the deep colours of the powders [26]. It is clear from Table 1 that metal loading enhances the recombination of the photogenerated electrons and holes. By increasing the metal content, k_r increases for each loaded metal with the exception of the samples containing copper or tungsten which reveal k_r values practically constant and almost independent on the amount of metal.

Table 1. Points of zero charge (pzc) and rate constants of electron-hole recombination (k_r) of bare and transition metal loaded TiO₂.

Sample	pzc (pH)	k_r (cm ³ ·ps ⁻¹)
TiO ₂	7.1	1.4
TiO ₂ /Co/0.3	7.5	2.3
TiO ₂ /Co/1.0	7.7	2.5
TiO ₂ /Co/2.0	7.9	3.0
TiO ₂ /Co/5.0	8.5	-
TiO ₂ /Cr/0.3	3.6	2.8
TiO ₂ /Cr/1.0	3.3	2.3
TiO ₂ /Cr/2.0	2.5	3.4
TiO ₂ /Cr/5.0	2.0	-
TiO ₂ /Cu/0.3	7.3	2.2
TiO ₂ /Cu/1.0	7.6	2.3
TiO ₂ /Cu/2.0	8.2	2.5
TiO ₂ /Cu/5.0	8.9	-
TiO ₂ /Fe/0.3	7.2	2.6
TiO ₂ /Fe/1.0	7.4	4.1
TiO ₂ /Fe/2.0	7.7	4.6
TiO ₂ /Fe/5.0	8.1	4.8
TiO ₂ /Mo/0.3	7.4	1.8
TiO ₂ /Mo/1.0	5.8	2.1
TiO ₂ /Mo/2.0	3.9	5.2
TiO ₂ /Mo/5.0	2.2	-
TiO ₂ /V/0.3	7.4	1.9
TiO ₂ /V/1.0	5.4	3.1
TiO ₂ /V/2.0	3.6	3.7
TiO ₂ /V/5.0	2.7	-
TiO ₂ /W/0.3	7.0	2.3
TiO ₂ /W/1.0	6.6	1.9
TiO ₂ /W/2.0	5.7	2.3
TiO ₂ /W/5.0	2.8	2.2

3.3. Effect of the transition-metal loading on the photocatalytic activity. Figure 3(a) shows the rate of formation of CO₂ as a function of the transition metal content. The rate of CO₂ evolution was determined during the photooxidation of ethanoic acid from the slope of the plots relative to the amount of product vs. irradiation time by considering the initial 1.5 h of irradiation. Instead, Figure 3(b) shows the initial zero order reaction rates of the apparent kinetics of disappearance of 4-nitrophenol obtained from the curves relative to the substrate concentration vs. reaction time. For both reactions, loading of any kind of transition metal generally gives rise to a decrease in the photocatalytic activity and this effect is more significant as the amount of loaded metal increases.

The photoreactivity results indicate that the TiO₂/Cu samples are always more active than the corresponding bare TiO₂ for the oxidation of ethanoic acid. The rate of CO₂ evolution increases by increasing the copper content up to 1% and reaches values not much lower than the maximum for higher loading. A possible explanation is that loaded Cu is reduced into a metallic state (Cu⁰) to act as a co-catalyst, increasing

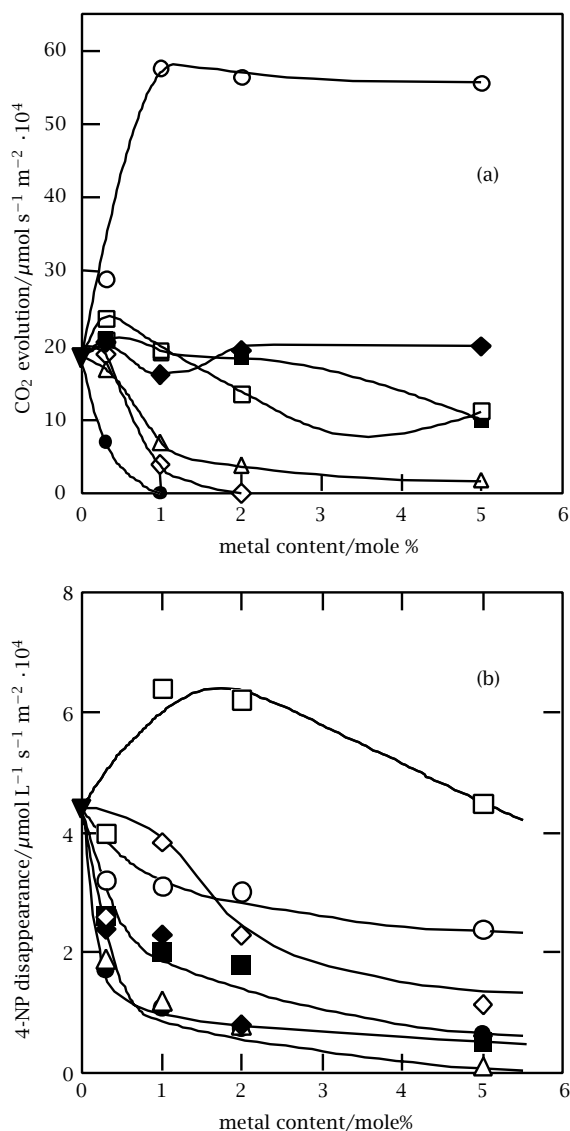


Figure 3. Rates of CO₂ evolution (a) and of 4-nitrophenol (4-NP) disappearance (b) versus the amount of metal content (%). Symbols as in Figure 2.

the photocatalytic activity of the support [26]. This hypothesis can be justified by the redox potential of Cu⁺/Cu (+0.1 V vs. SCE) which is more positive than the conduction band of TiO₂. Moreover the colour of the TiO₂/Cu suspensions in aqueous ethanoic acid turned from ivory to black during the photoirradiation.

As for the 4-nitrophenol photodegradation, the activity of TiO₂/W/0.3 is slightly lower than that of TiO₂ while the reaction rates of the other TiO₂/W samples are higher than that of the support with a maximum for TiO₂/W/1. The beneficial effect of tungsten on the photoactivity of TiO₂ has been explained by the formation of W⁵⁺ species by means of transfer of photoproduced electrons from TiO₂ to W⁶⁺. Subsequently W⁵⁺

oxidises to W⁶⁺ by transferring electrons to adsorbed O₂ [10, 12].

The observed different behaviour exhibited by the TiO₂/Cu samples when they are used to photodegrade ethanoic acid and 4-nitrophenol could be explained by taking into account that the formation of Cu⁰ is greatly favoured for high concentrations of organic molecules, acting as hole traps. It is worth noting that the runs for 4-nitrophenol degradation were carried out with a very low initial concentration of this organic substrate. Moreover, the pzc's of the TiO₂/Cu samples (see Table 1) are quite basic so that the interaction between surface of the catalyst and ethanoic acid (an acid stronger than 4-nitrophenol) is favoured. On the contrary, the interaction with 4-nitrophenol could be more important for the TiO₂/W samples whose pzc values are rather acid.

It is not easy to rationalize the low efficiencies obtained in the presence of all the other dopants as many physicochemical and/or intrinsic electronic factors can influence beneficially or detrimentally the photocatalytic activity of the doped TiO₂ powderds [17].

3.4. Dependence of the photocatalytic activity on k_r . The lifetime of trapped electrons has been related to the photocatalytic activity of bare and metal-loaded TiO₂ powders [19]. As a general trend, the longer the lifetime of trapped electrons, the higher the photocatalytic activity of the samples.

Figure 4 shows the correlation between the rates of the reactions (a) and (b) and the values of k_r of the various samples, reported in Table 1. For the oxidation of ethanoic acid (Figure 4(a)), the relation between photoactivity and electron-hole recombination rate is rather confusing due to the high photoefficiencies of the TiO₂/Cu samples whose k_r values are also quite similar each other. By removing the results of these samples from the figure, the reaction rate of CO₂ production appears to be almost independent of k_r .

According to a simple kinetic model [26], it is expected that the e⁻-h⁺ recombination is detrimental to the photocatalytic activity unless the photogenerated pairs react efficiently with the surface adsorbed substrates. If the decomposition of ethanoic acid is carried out under an Ar atmosphere [26], a k_r dependence similar to that of reaction (b) is obtained, indicating that the presence of O₂ makes negligible the influence of the electron-hole recombination. By presuming that the reaction proceeds via oxidation of surface adsorbed ethanoic acid by h⁺ and reduction of O₂ by e⁻, probably the rate of CO₂ evolution does not depend on k_r because, in the presence of air, the surface-adsorbed O₂ reacts with e⁻ before its recombination. Obviously, it cannot be excluded that many other factors control the rate of the reaction.

The plot of Figure 4(b) is fairly scattered but it can be noticed that, with increasing k_r , the rate of 4-

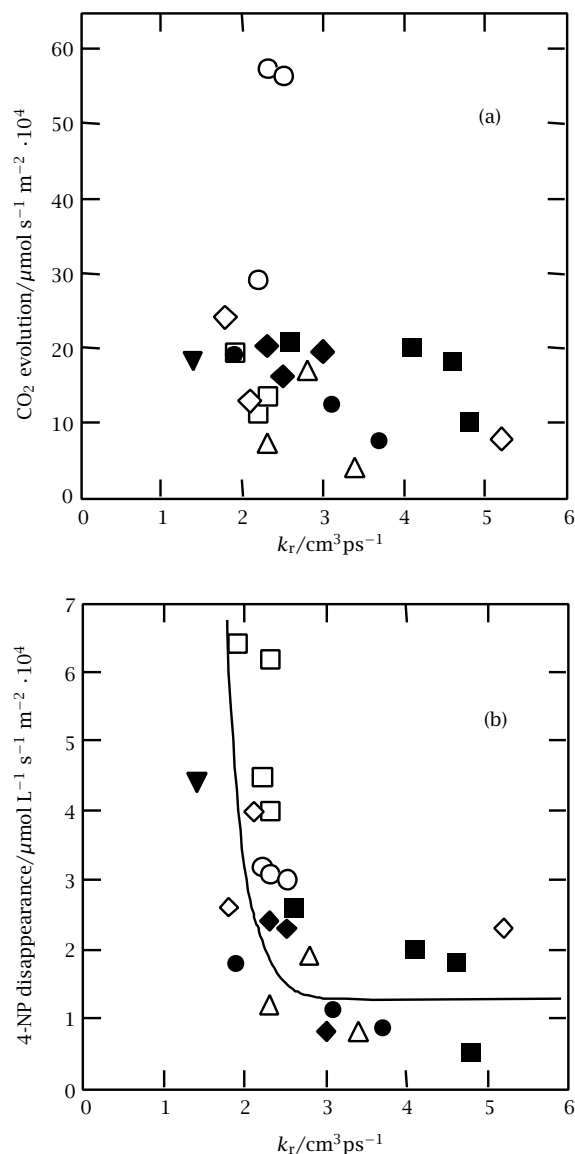


Figure 4. Relation between k_r values and the rates of CO₂ evolution (a) and of 4-nitrophenol (4-NP) disappearance (b). Symbols as in Figure 2.

nitrophenol disappearance first significantly decreases and then becomes practically constant. By assuming that the photoactivity of the samples is inversely proportional to the increase in k_r [26], this means that the net activity of 4-nitrophenol photodegradation is dominated by the electron-hole recombination rate when the k_r values are relatively low whereas the reaction rate becomes independent of k_r when the recombination of the photogenerated pairs is too fast.

An explanation for the two different k_r dependences can be based on the assumption that the distance between the place where e^-h^+ pairs form and react with the substrates depends on the type of photoreaction

[26]. The reaction of 4-nitrophenol degradation proceeds through several steps and numerous intermediates so that oxidation and reduction by h^+ and e^- likely occur at separate sites. It seems reasonable to infer that the rate of the reaction depends on k_r since e^- (or h^+) must migrate in the bulk or on the surface of the catalyst particles. Instead, the oxidation of ethanoic acid and the reduction of O₂ occur at neighbouring sites so that the scarce dependence of the rate of CO₂ evolution on k_r could be justified by a negligible migration of e^- (or h^+).

The different relations between k_r values of the various samples and the rates of the reactions (a) and (b) can be also due to the different experimental conditions under which the reactions (a) and (b) were carried out. In fact, ethanoic acid, due to its high concentration, can work as an efficient hole trap, levelling the influence of the recombination rates of the various powders.

ACKNOWLEDGEMENTS

The authors wish to thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Italy) and the Ministry of Education, Science, Sports and Culture (Japan) for the financial support.

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