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Influence of metallic species on TiO_2 for the photocatalytic degradation of dyes and dye intermediates

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Abstract

The present work is focused on the influence of metal salts on the photocatalytic efficiency of TiO_2 for the elimination of two azo dyes: acid orange-7 (AO-7), tartrazine and a dye intermediate: 3-nitrobenzenesulfonic acid (3-NBSA). A beneficial effect of the presence of metallic species was observed only with samples containing silver. In contrast when compared with Ag^+, Cu^{2+} and specifically $VO_3{}^-$ showed an inhibiting effect on the kinetics of degradation for the three substrates studied. No significant decrease in the initial concentration of the substrates was observed for direct phototransformation in sunlight during the same time.

Keywords: Photocatalysis; Silver; Copper; Vanadate; Acid orange-7; Tartrazine; 3-NBSA

1. Introduction

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Dyes are extensively used and hence wastewaters discharged in rivers or public sewage treatment plants are highly coloured and contaminated. Photocatalysis on TiO_2 was often proposed to eliminate these pollutants. Its efficiency may be significantly modified by the presence of metals.

The addition of a low percentage of metal was often proposed to improve the photocatalytic activity of TiO_2. The metal may be introduced through different ways.

- Doping, i.e. molecular combination of metal oxide in the lattice of TiO_2. This process is expected to modify the band gap of the photocatalyst.
- Metallisation, i.e. deposition of noble metal on TiO_2 crystallites.
- Impregnation of TiO_2 with a salt of metal followed by evaporation, i.e. deposition of small amount of salt on TiO_2 surface.
- Addition of low concentrations of transition metal to the solution of substrate to be treated.

Several metals were used for doping especially Pt°, Li^+, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ce^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Al^{3+} [1,2]. Generally they have no beneficial effect on the photocatalytic degradation of phenol probably because they decrease the band gap. The presence of Pt° do not change much the rate of disappearance of phenol, but it reduces the further transformation of hydroquinone. The presence of Mn^{2+}, Ce^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+} and Al^{3+} ions (5 mol% M^{n+}: Ti^{4+}) in TiO_2 layer supported on glass fibres has a detrimental effect on the photoactivity.

Platinisation of titania has been proposed as early as 1978 for photocatalytic transformation of acetic acid [3]. It was also used for the degradation and dimerisation of alcohols [4] for the *N*-alkylation of ammonia and amines [5], or the oxidation of hydrocarbons [6].

The presence of transition metal may increase the photocatalytic activity either by scavenging e^- that reduces the recombination of charges and therefore favours the formation of $^\bullet OH$, or by the intermediate of Fenton type reactions:

$$M^{n-1} + H_2O_2 \rightarrow M^n + {}^\bullet OH + OH^-$$

However high concentration of metal may have a detrimental effect either by a competitive trapping of oxidising species h^+ and $^\bullet OH$, or by filter effect when salts significantly absorb in UV range (Cu^{II}, Ni^{II} and Fe^{II}). Besides the redox potentials of Cu/Cu^+, Cu^+/Cu^{2+} and Fe^{2+}/Fe^{3+} permits the formation of photocurrent. With Pt and Pd salts deposition of Pt° and Pd° may occur on the particles of TiO_2 [7]. Different processes may be involved according to the conditions. Okamoto et al. [8] reported that the

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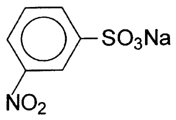
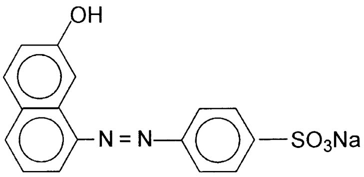
influence of Cu^{2+} may be positive or negative according to the concentration. It was also reported by Kiriakidou et al. [9] that the addition of Ca^{2+} to titania induces a little decrease of the photocatalytic degradation of acid orange-7 (AO-7), whereas the presence of W^{6+} has a significant positive effect only for small percentages of W^{6+}.

Then it is difficult to access the influence of transition metals on photocatalysis and experiments are necessary to point out the effect of these metals. The present work is focused on the influence of metals Ag^{+}, Cu^{2+} and VO_3^{-} (vanadate) on the photocatalytic degradation of two typical azo dyes used in dyeing industry AO-7 and tartrazine (Tart) and one nitroaromatic dye intermediate 3-nitrobenzenesulfonic acid (3-NBSA).

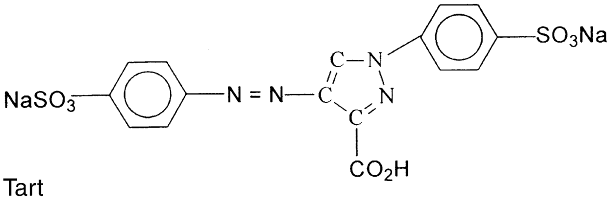
It was experimentally proved that these substrates are photostable in the absence of photocatalyst. 3-NBSA was chosen since it is highly soluble in water and then it does not adsorb much on titania. Besides the presence of nitro group reduces the reactivity with $^{\bullet}OH$ [10].



(3 - NBSA)



(AO -7)



Tart

2. Materials and methods

2.1. Photocatalysts

Three kinds of TiO_2 were used as slurry $2\,g\,l^{-1}$. Their main physico-chemical characteristics are reported in Table 1. The precursors for salt deposition were $CuSO_4\cdot 6H_2O$ from S.D. Fine Chemicals, $AgNO_3$ from Aldrich and ammonium *meta*-vanadate NH_4VO_3 from Fluka.

The amount of metal was chosen in order to obtain 1% molecular metal dopant with respect to TiO_2. Deposition was obtained by wet impregnation method. The same procedure was adoped for the three metals with this difference that with vanadate water has to be heated at 70 °C to dissolve the salt. After allowing to stand P 25 titania powder with the solution of salt during 24 h, water was evaporated by heating at 100 °C for 12 h. The dried solids were normally ground in an agate mortar and calcined at 400 °C for 6 h.

Table 1
Physico-chemical properties of TiO_2 used

Photocatalyst	P 25	PC 50	PC 500
Origin	Degussa	Millennium	Millennium
Anatase (%)	70–80	100	100
BET surface area ($m^2\,g^{-1}$)	55 ± 5	45 ± 5	>250

2.2. Substrates

Acid orange-7 was purchased from ACROS, tartrazine from S.D. Fine Chemicals and 3-NBSA sodium salt (>95%) from Fluka. Water used for solutions was purified by Milli-Q system (Millipore) and controlled by its resistivity (>18 MΩ cm).

2.3. Irradiations

The device used for irradiation is described elsewhere [11]. It consists of a vertical Pyrex tube (20 mm i.d.) with a water cooling jacket. The light source is a fluorescent lamp TLD 15 W/05 emitting between 300 and 450 nm. Both lamp and reactor are located along both focal axes of a cylindrical mirror with elliptic base. Usually 60 ml of solution with 120 mg of TiO_2 were irradiated under magnetic stirring to maintain the titania in suspension. In this device the number of photons received is almost proportional to the volume irradiated and consequently sampling do not significantly modify the kinetics of the reaction. Evaporation was found to be negligible. To quantify the decrease of the concentration a sample of 2 ml was taken at regular intervals of time and filtered through Millipore 0.45 μm filters.

2.4. Analyses

The disappearance of AO-7 and Tart were monitored by their UV-Vis absorption. The former has a maximum absorption at $\lambda_{max} = 485$ nm with molecular absorption coefficient $\varepsilon = 21400\,M^{-1}\,cm^{-1}$. For the latter $\lambda_{max} = 455$ nm with an $\varepsilon = 6400\,M^{-1}\,cm^{-1}$. During irradiation the UV spectra decrease without deformation that means there is no formation of intermediates absorbing in the same range. It is different with 3-NBSA, which absorbs at shorter wavelength ($\lambda_{max} = 260$ nm). The disappearance was monitored by HPLC using a C_{18} column with a mixture MeOH/water (50:50) as the eluent. Tetrabutylammonium hydrogen sulphate (5×10^{-3}) was added to water to obtain a good resolution of the chromatogram.

2.5. Adsorption studies in the dark

Adsorption studies in the dark were performed using the aqueous solutions of dye at two different concentrations with TiO_2 alone and metal impregnated TiO_2 for overnight at 25 °C. Then, the solutions were filtered through a Millipore

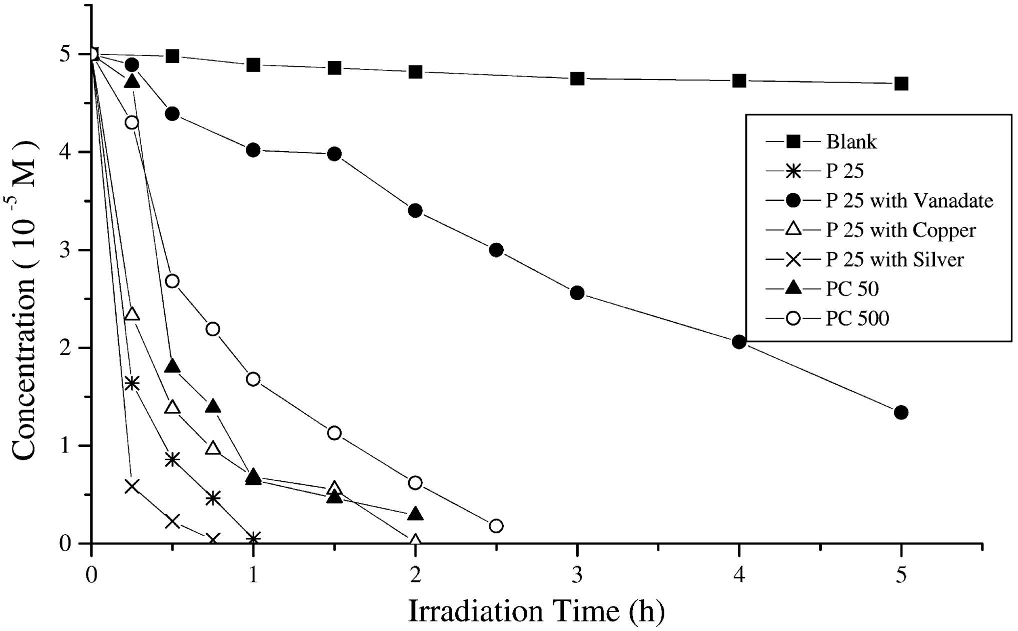


Fig. 1. Photocatalytic transformation of AO-7 on TiO_2 and metal impregnated TiO_2 catalysts. Initial concentration: 5×10^{-5} M.

0.45 μm filter and the reminiscent dye concentration was measured by UV-Vis spectrophotometer.

3. Results

3.1. Direct photolysis

Before studying the photocatalytic transformations it was observed experimentally that direct photolysis of substrates is very slow in sunlight.

A solution of 3-NBSA 4×10^{-5} M was exposed to sunlight in Pyrex vessel. After 1 month (November) only 1.5% of 3-NBSA disappeared. With AO-7 and Tart solutions of 5×10^{-5} M were exposed to sunlight in the similar way as above and negligible transformation was observed after 1 month (June).

3.2. Adsorption

It is likely that the adsorption of the dye is an important parameter in the photocatalytic process. In our experimental

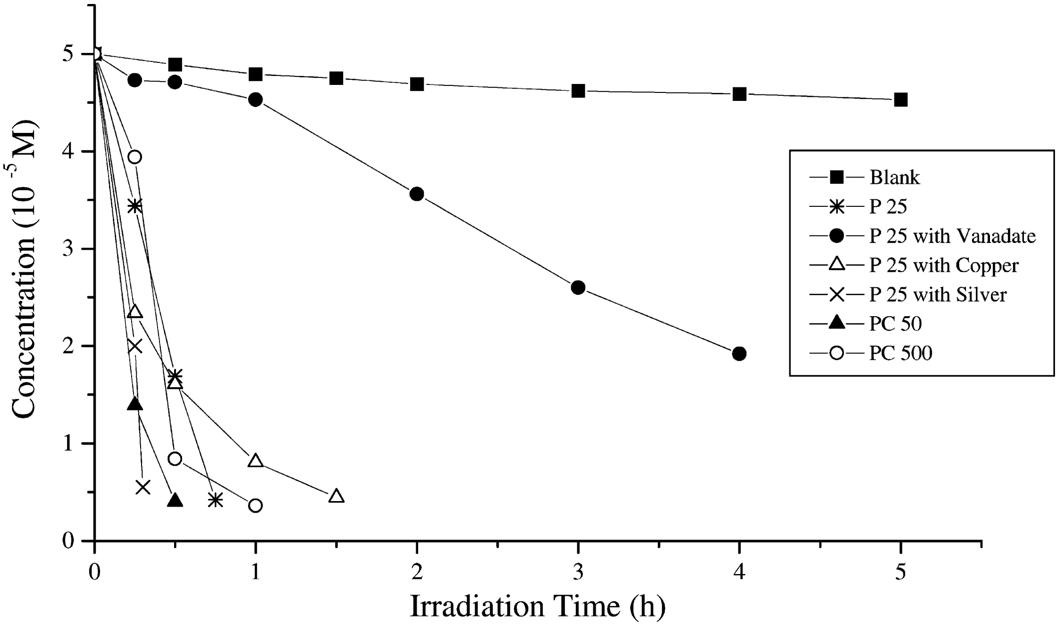


Fig. 2. Photocatalytic transformation of tartrazine on TiO_2 and metal impregnated TiO_2 catalysts. Initial concentration: 5×10^{-5} M.

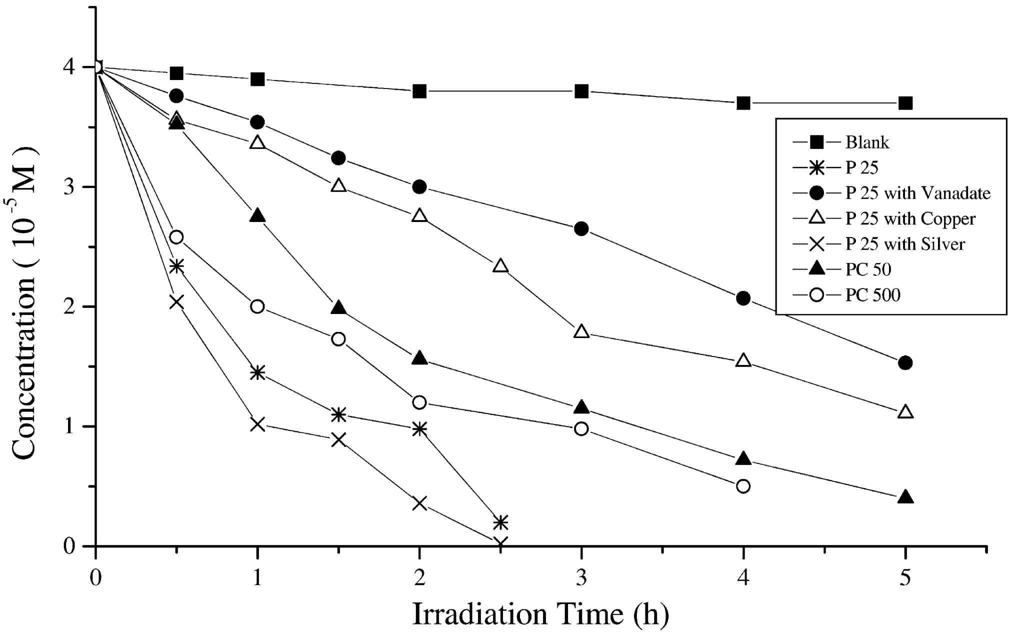


Fig. 3. Photocatalytic transformation of 3-NBSA on TiO_2 and metal impregnated TiO_2 catalysts. Initial concentration: 4×10^{-5} M.

conditions there was no observable decrease of concentration when the adsorption was carried out in the dark for all the catalysts used.

3.3. Photocatalytic degradation

3.3.1. Acid orange-7

A 60 ml solution of AO-7 (5×10^{-5} M) was photodegraded in artificial light (300–450 nm) using a slurry reactor with different kinds bare catalysts (Degussa P 25, Millennium PC 50 and PC 500) and P 25 impregnated with Ag^+, Cu^{2+} and $VO_3{}^-$. Results are reported in Fig. 1. It clearly appears that the best efficiency is obtained with Ag^+ impregnated photocatalysts. TiO_2 P 25 with vanadate leads to a less efficient photocatalysis. PC 500 is less efficient than PC 50 in spite of a larger surface area.

3.3.2. Tartrazine

The efficiency of different titania and metal impregnated titania were also compared using 60 ml solution of tartrazine (5×10^{-5} M) as the substrate (Fig. 2). This substrate did not show any significant disappearance without catalyst (“blank” in Fig. 2). Results are consistent with those obtained above with AO-7. Tartrazine followed a similar degradation pattern with all the catalysts. As previously observed above, vanadate has a detrimental influence on photocatalysis and there is only little influence of Cu^{2+}. It can also be noted that P 25 is more efficient than PC 50, but it is different for PC 500 which is more active than PC 50.

With all the catalysts the transformation of tartrazine is more rapid than the transformation of AO-7.

3.3.3. 3-Nitrobenzenesulfonic acid

It appears from Fig. 3 that the transformation of 3-NBSA (4×10^{-5} M) is much slower than the degradation of both dyes with all catalysts considered. The enhancing effect of Ag^+ was also observed as well as the detrimental influence of vanadate. With bare photocatalyst P 25 is more active than PC 50 but less than PC 500.

4. Discussion

The enhancing effect of Ag^+ may be explained by its ability to trap electrons:

$$Ag^+ + e^- \rightarrow Ag^\circ$$

This process reduces the deactivation, i.e. recombination of charges and favours the oxidation of substrate. Actually it was observed that the catalyst slightly darkens during the irradation.

With vanadate metal is included in an anion that traps positive holes and inhibits the reactions of oxidation. The unstable intermediate VO_3 is expected to be regenerated by electrons of conduction band. The behaviour of Cu^{2+} is more complex. Cu^{2+} may scavenge electrons with formation of Cu^+, but the latter can be reoxidised by positive holes or hydroxyl radicals. The first step enhances the oxidation of substrate, the latter inhibits it. Then it is not surprising that Cu^{2+} has only a minor influence on the photocatalytic activity of TiO_2.

Besides it was observed that the photocatalytic oxidation of both dyes is more efficient than the degradation of

3-NBSA. Actually the oxidation of dyes by $^{\bullet}$OH is expected to be almost diffusion controlled whereas it was recently proved [10] that the rate constant of the reaction $^{\bullet}$OH with 3-NBSA is approximately ($6.55 \times 10^8\,M^{-1}\,s^{-1}$), 10 times less than its rate constant with benzenesulfonic acids without nitro group ($3.0–5.6 \times 10^9\,M^{-1}\,s^{-1}$). This inhibiting effect is due to the electron-withdrawing effect of NO_2 group that unfavours electrophilic oxidations.

5. Conclusion

With the three substrates considered P 25 is more active than PC 50, but in the case of tartrazine PC 500 has same efficiency than P 25. There is no evident relationship between surface area and photocatalytic activity.

The deposition of metallic salts on TiO_2 (1% metal/TiO_2) can have completely different effect according to the speciation of the metal. Silver salts have enhancing effect since they are easily reducible and act as electron traps. In contrast vanadate has a detrimental influence due to its anionic form. Cu^{2+} has no significant influence. The presence of nitro group on aromatic ring reduces the photocatalytic oxidation.

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