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A proof of the direct hole transfer in photocatalysis: The case of melamine

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ABSTRACT

The photoinduced transformation of 2,4,6-triamino-1,3,5-triazine (melamine) was studied by using different advanced oxidation technologies under a variety of experimental conditions. The systems involving homogeneous hydroxyl radicals, as generated by $H_2O_2/h\nu$, Fenton reagent, and sonocatalysis are ineffective. However, melamine is degraded under photocatalytic conditions or by $SO_4^{\bullet-}$ ($S_2O_8^{2-}/h\nu$). The time evolution of long-living intermediates, such as 2,4-diamino-6-hydroxy-1,3,5-triazine (ammeline) and 2-amino-4,6-dihydroxy-1,3,5-triazine (ammelide), has been followed, being 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid) the final stable product. During both photocatalytic and $S_2O_8^{2-}/h\nu$ experiments, in the early steps, a fairly stable intermediate evolving to ammelide is observed in a large extent. This intermediate was identified as 2,4-diamino-6-nitro-1,3,5-triazine. This indicates that the primary photocatalytic event is the oxidation of the amino-group to nitro-group through several consecutive fast oxidation steps, and that a hydrolytic step leads to the release of nitrite in solution. To elucidate the nature of the oxidant species hole scavengers such as methanol and bromide ions were added to the irradiated TiO_2. They completely stop the degradation, whereas chloride and fluoride ions decrease the degradation rate.

The study of the photocatalytic degradation rate of melamine at increasing concentrations using two different commercial titanium dioxides, such as P25 and Merck TiO_2, showed an intriguing behavior. A drastic abatement of the melamine transformation rate was observed when coagulation of the P25 slurry occurs due both to the pH change and melamine concentration effect that increase melamine adsorption. In the presence of TiO_2 (Merck) the melamine initial degradation rates are significantly lower than those observed in the presence of P25 but are not depressed at larger concentrations. The experimental evidences (e.g., absence of melamine adsorption onto TiO_2 surface at low concentrations or at acidic pH or due to the catalyst surface texture, and the lack of reactivity toward $^{\bullet}OH$ free and bound) suggest that the effective photocatalytic mechanism is based on an outer sphere direct hole transfer to the melamine. Its formal potential lies in the range 1.9–2.3 V vs NHE. Then, the photodegradation of melamine is an efficient tool to evaluate the direct hole transfer ability of a photocatalyst.

1. Introduction

The photocatalytic transformation of several *s*-triazine derivatives has been extensively investigated [1–3]. *s*-Triazine derivatives have the unique property to lose easily the substituents, but to retain the *s*-triazine ring till to the formation of 2,4,6-trihydroxy-1,3,5-triazine (cyanuric acid), which is stable to further photocatalytic oxidation [1]. Interestingly, other oxidation processes like UV/H_2O_2 and Fenton reaction lead to stable products that retain the amino group (e.g., from atrazine ammeline is formed) and no cyanuric acid is observed [4,5]. These evidences suggest to study the behavior of melamine (2,4,6-triamino-1,3,5-triazine) under photocatalytic conditions and in $^{\bullet}OH$ generating systems.

A preliminary investigation about the UV/TiO_2/H_2O_2 melamine degradation was proposed [6] where a not complete mineralization was reported because of the formation of cyanuric acid as last product. An increase of the toxicity during melamine degradation was observed suggesting an undesirable increase of toxicity also during melamine degradation in living tissues. Nothing was reported about the nature of intermediates during the first steps of the photocatalytic process.

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In the present paper the photocatalytic transformation of melamine by using different oxidation processes under a variety of conditions is reported. Attention is devoted to the mechanism of oxidation, and in particular to the role of hydroxyl radical vs direct hole oxidation mechanism. In TiO_2 photocatalysis the role of bound or free $^{\bullet}OH$ mediated oxidation vs direct hole transfer oxidation has been extensively debated [7] and the elucidation of the significance of these pathways has a fundamental importance in the understanding and control of photocatalytic processes. Evidences in support of both mechanisms have been obtained [8,9]. As far as mechanism is concerned, hydroxyl radical addition or direct electron abstraction can be undistinguishable based on the detected intermediates for most of the substrates.

Some experimental evidences reported on phenol, formate, hydrogen peroxide and glycerol photocatalytic transformations shed some light on these possible pathways [10,11]. Moreover, they gave insights into the energetics of the surface traps for holes, including also the states associated to adsorbed substrates, and the possibility of water oxidation. It was outlined how the intrinsic and extrinsic surface properties can affect the selectivity of the photocatalytic degradation toward different substrates [12]. Moreover, changes in the extrinsic surface properties, and in particular the adsorption of redox stable ions, influence the relative role of the different paths during the photocatalytic process. Particular attention was devoted to the specific adsorption of fluoride ions (ligand exchange reaction between the surface hydroxy groups and the fluoride ions [11]), which promotes the phototransformation of substrates that react predominantly via $^{\bullet}OH$ mediated oxidation (e.g., phenol) [7,13], while decreases the degradation rate of substrates (e.g., hydrogen peroxide, catechol) that react predominantly by direct hole transfer mechanism because hinders their specific adsorption [11,14–16]. Depending on the substrates, hydroxyl radicals, direct hole transfer (inner or outer sphere) or reductive pathways may operate as initial step and be active all together during the overall degradation process.

A substrate with a high monoelectronic oxidation potential, not reactive toward $^{\bullet}OH$ radicals and poorly adsorbed onto TiO_2 can help to probe a mechanism that involves a direct hole transfer (likely promoted by shallow surface traps) in photocatalysis. To get information on the hydroxyl radical mechanism, experiments with homogeneous $^{\bullet}OH$ generating systems were performed. Moreover, attention was devoted to the study of the differences in the photocatalytic activity of TiO_2 P25 and TiO_2 Merck, two different commercial powders with marked differences in their surface features, to highlight the role of the surface properties on the photocatalytic process mechanism. Considering that cyanuric acid is the final product of melamine transformation, this allowed investigating on the mechanism of $-NH_2$ substitution. Previous studies showed that under photocatalytic conditions the substituents containing nitrogen are redox interconverted ($-NH_2 \rightarrow -NHOH \rightarrow -NO \rightarrow -NO_2$) [17].

2. Experimental

2.1. Materials and reagents

Melamine (99+%, Aldrich), Cyanuric acid (CYA) (98%, Aldrich) were used without further purification. Ammeline (AN) and Ammelide (AD) were synthesized with the procedure described elsewhere [1]. All other chemicals were commercially available, with at least analytical purity, and used without further purification. TiO_2 P25 by Evonik (formerly Degussa, SSA_{BET} area ca $50\,m^2\,g^{-1}$, mixture rutile:anatase 20:80) and TiO_2 by Merck (SSA_{BET} area $10\,m^2\,g^{-1}$, anatase 100%) were irradiated in aerated aqueous suspension for at least 12 h and washed with ultrapure water in order to avoid interference from organic impurities and inorganic ions adsorbed on the photocatalyst. The physical and photochemical properties of the used photocatalyst are reported elsewhere [18].

Aqueous stock solutions of Melamine ($1000\,mg\,dm^{-3}$), AN ($20\,mg\,dm^{-3}$), AD ($20\,mg\,dm^{-3}$) and CYA ($1000\,mg\,dm^{-3}$) are fairly stable and last for weeks.

All the aqueous solutions were prepared employing ultrapure water obtained with a MilliQ plus apparatus (TOC = 2 ppb, conductivity 18.2 MΩ cm).

2.2. Degradation experiments

The slurries for photocatalytic experiments were prepared by suspending with sonication the required amount of photocatalyst powder and addition of the needed amount of the aqueous stock solution of substrate. Being 5.5 the natural pH of a TiO_2 suspension ($500\,mg\,dm^{-3}$) the pH of the slurries before irradiation was adjusted by adding drops of 1 M solutions of NaOH or $HClO_4$ as required.

The irradiation experiments were carried out in Pyrex glass (cut-off at 295 nm) or quartz cylindrical cells (4.0 cm diameter, 2.3 cm height) containing 5 mL of the aqueous suspension of the photocatalyst powder and substrate, using a Philips TLK 40 W/05 fluorescent lamp (Phillips, Eindhoven, Nederland) in standard conditions ($33\,W\,m^{-2}$). This lamp emits a band 60 nm wide, centered at 360 nm (the complete spectrum is reported in Ref. [19]). Homogeneous degradation with the H_2O_2 or $S_2O_8{}^{2-}$/UV systems was carried out in quartz cells, using a Philips 20 W low pressure mercury lamp, emitting at 254 nm. The cell apparatus was described elsewhere [1]. The total photon fluxes in the cells were 7.1×10^{-6} and 7.9×10^{-8} Einstein min^{-1} in the 200–420 nm range with the fluorescent and the mercury lamp, respectively (ferrioxalate actinometry). The cell temperature during irradiation was $30 \pm 3\,^{\circ}C$. The experiments in the absence of air were prepared purging with He the closed irradiation cells containing either the TiO_2 suspension or water. Then, the required volume of substrate stock solution and, when relevant, the hydrogen peroxide solution were injected in the cell with a microsyringe. During irradiation the slurries were magnetically stirred.

Sonication experiments were conducted with a Branson Sonifier B-15 equipped with standard horn and tip, and a stainless steel sealed 50 mL chamber with cooling jacket. The output setting was adjusted to obtain a 65 W output at 20 kHz. The temperature was maintained at 25 °C.

Degradation runs with the Fenton reagent were carried out in the presence of H_2O_2 50 mM and $FeSO_4$ 1 mM at pH 2 (H_2SO_4). The reaction was stopped by adding methanol.

2.3. Analytical determinations

The HPLC determinations were carried out with a Hitachi Elite Lachrom L2200, equipped with a Diode Array Detector (Hitachi L-2455), on the filtered (Millex HV 0.45 μm, Millipore) irradiated aqueous samples.

Melamine, AN, AD and CYA were quantified with ion pair chromatography with a bonded phase octadecylsilica column (LiChrospher R100-CH 18/2 by Merck, 250 mm length, 10 mm i.d., 5 μm packing); the mobile phase was 0.01 M sodium hexane sulfonate (Aldrich ion-pair reagent 99+%) and 0.014 M H_3PO_4 dissolved in water/CH_3CN 95/5 at 1 mL min^{-1}. Retention times were: melamine 7.8 min, AN 6.8 min, AD 3.1 min and CYA 2.3 min. The detection was carried out at 200 nm for melamine and CYA, at 221 nm for AD and at 229 nm for AN to optimize the analytical sensitivity for each compounds.