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Different photocatalytic fate of amido nitrogen in formamide and urea

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In the comparison of formamide and urea photocatalytic degradation, despite their similar structures, the final fate of bound nitrogen under illumination with TiO_2 has shown a different behaviour; both the rate and the ratio of NH_4^+ and NO_3^- ion evolution seem not to be linked to the initial nitrogen oxidation state, but to the carbon oxidation state.

Light activated processes on TiO_2 have been widely studied and employed, both in the abatement of widespread classes of pollutants and in gaining information on naturally occurring transformations. Nevertheless, despite their extensive applications, several mechanistic aspects are still unexplained. One of these points is represented by the fate of bound nitrogen, for which the transformation into inorganic ions (*i.e.* ammonium and nitrate) has been observed but the detailed mechanism of their formation has not been elucidated until now. The comprehension of all the possible processes involved in the natural evolution of nitrogen-containing compounds is extremely important not only because nitrogen constitutes a key element of nutrient cycling but also because a large number of anthropogenic compounds contain one or more nitrogen atoms. The final fate of organic nitrogen under photocatalytic processes[1] has been reported to be related essentially to the initial oxidation state of nitrogen in the organics, to the presence/absence of oxygen and, in a few cases, to the structure of the organic compound (*e.g.* 4-nitrosophenol *vs.* nitrosobenzene).[2–11] In the present communication, the fate of nitrogen initially present as an amido group under photocatalytic conditions is reported, showing different ratios of $[NH_4^+]/[NO_3^-]$ for formamide with respect to urea.

The basic principles of photocatalysis have been extensively discussed elsewhere[12–15] and will be only briefly presented here. The primary photochemical event, following the near-UV light absorption by TiO_2 ($\lambda > 380$ nm) is the generation of electron/hole pairs in the bulk of the semiconductor. The charge carriers can either recombine or migrate to the surface where they are ultimately trapped: the electrons as Ti(III) and the holes as surface radical hydroxyl groups. If electron acceptors or electron donors are present at the surface, interfacial electron transfer may also occur.

The irradiation of the single species was carried out on 5 ml of aqueous suspension containing 8×10^{-4} M organic compound and 0.5 g L^{-1} of catalyst, using a 1500 watt Xenon lamp (Solarbox, CO.FO. MEGRA, Milan, Italy) simulating AM1 solar light and equipped with a 340 nm cut-off filter. The content of the cell was filtered through a 0.45 μm cellulose acetate filter (Millipore HA) and analyzed by the appropriate analytical technique (either HPLC or ion chromatography).

The disappearance of $HCONH_2$ and $CO(NH_2)_2$ at pH 5.4 ± 0.1 on TiO_2 catalyst occurs with kinetics strongly depending on the initial compound, the observed rate constants being 7.6×10^{-2} min^{-1} and 2.0×10^{-3} min^{-1}, respectively. The homogeneous rate constant for $^{\cdot}OH$ radicals toward urea is reported to be 7.9×10^5 M^{-1} s^{-1},[16] whereas a value is not available for formamide. If we assume the value quoted for formic acid as a reference (1.4×10^8 M^{-1} s^{-1}), a close parallelism can be observed between free $^{\cdot}OH$ and $\equiv Ti{-}^{\cdot}OH$. Confirmation of this hypothesis comes from experiments performed on urea and formamide with H_2O_2 under illumination at 254 nm and on a fluorinated titanium surface, as will be presented in a forthcoming work.

Fig. 1 illustrates the evolution of NH_4^+ and NO_3^- ions. In the case of formamide a quasi steady-state condition is reached after 1 hour, as shown in Fig. 1A, with a ratio of $[NH_4^+]/[NO_3^-] \cong 2.0$; at longer irradiation times only minor conversion of NH_4^+ into NO_3^- is observed, as depicted in the Fig. 1A inset. In the case of urea, a quasi steady-state condition is reached only after *ca.* 20 h with a ratio of $[NH_4^+]/[NO_3^-] = 0.5$.

As, in both cases, the nitrogen oxidation state is -3, the remarkable differences in the degradation rate and in the final nature of nitrogen both originating from an amido group can be rationalized by considering the carbon oxidation state. Noting that the C atom in the urea structure has a +4 oxidation state (and no abstractable C–H bonds are present), $^{\cdot}OH$ attack is then occurring at the $-NH_2$ moiety and a sequence of O_2 addition and further $^{\cdot}OH$ reactions leads to the large predominance of nitrate (probably

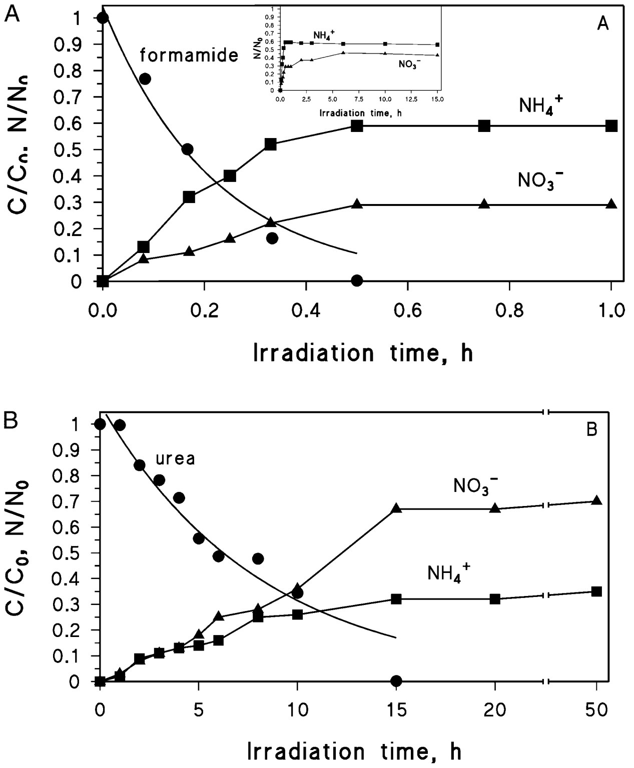

Fig. 1 Disappearance of substrates and evolution of nitrate and ammonium ions during the formamide (A) and urea (B) (0.83 mM) degradation as a function of irradiation time on TiO_2 0.5 g L^{-1}. Urea and formamide have been detected by HPLC, equipped with a Merck Lichrospher 100 CN (10 μm) column and detection at 194 nm by adopting phosphate buffer 1×10^{-2} M at pH 3 as eluant. The determination of inorganic ions has been performed by adopting a Dionex instrument equipped with a conductimeter detector. Nitrate ions have been detected by using a AS9HC (Dionex) anionic column and a buffer solution of $NaHCO_3$ 12 mM and K_2CO_3 5 mM at a flow rate of 1 ml min^{-1}; for ammonium ions, a CS12A (Dionex) column and 25 mM metansulfonic acid as eluant have been adopted.

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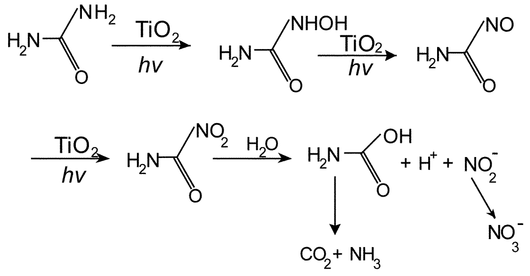
through release as nitrite, which is known to be rapidly oxidized to nitrate in these conditions).

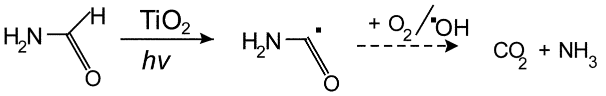
Tentatively, the formation of nitrate ions could be reached through the sequence (1):



(1)

Beyond the nitrate formation, 30% of the nitrogen is converted into ammonium ions. Since there is negligible formation of ammonium from nitrite and nitrate in these conditions, ammonium ions are probably originating from hydrolysis of some intermediates (radical or molecular, *e.g.* carbamic acid). The ratio $[NH_4^+]/[NO_3^-]$ suggests that parallel to sequence (1), $^{\cdot}OH$ attack also occurs to the second $–NH_2$ group.

A different mechanism is operating for $HCONH_2$. The carbon oxidation state of +2 and the presence of a C–H bond is presumably favouring the $^{\cdot}OH$ attack, generating $^{\cdot}CONH_2$ as the initial radical species. In this case, the main pathway could be represented by the radical attacks as illustrated below:



(2)

However the NO_3^- evolution suggests a possible attack at the $–NH_2$ group through a sequence like (1). A lack of ~10% of the stoichiometric nitrogen amount is observed, similarly to the cases of cyanate, hydrazine and azo-derivatives.[17,18]

In conclusion, the described data show an interesting correlation between the carbon oxidation state and the final fate of bound nitrogen, suggesting that the fate of the nitrogen (in the −3 oxidation state in both compounds) is governed by the initial oxidation state of carbon (+4 in urea and +2 in formamide).

Future developments have to consider the influence of substituents on the amino group, so evaluating the variation induced by the substitution of the hydrogen atoms by electron attractor and/or donor groups on the fate of the bound nitrogen and organic carbon mineralization.

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