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ScienceDirect
Catalysis Today 129 (2007) 16–21
CATALYSIS TODAY
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Photocatalytic oxidation mechanism of benzonitrile in aqueous suspensions of titanium dioxide

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Available online 31 July 2007

Abstract

The photocatalytic oxidation of benzonitrile was carried out in aqueous suspensions (pH 11) of commercial polycrystalline TiO_2 (Merck and Degussa P25) irradiated by ultraviolet light.

The rate of decomposition was dependent on the concentration of benzonitrile and followed a pseudo-first order kinetics. The complete mineralization of a 0.70 mM benzonitrile solution was achieved in ca. 8 h by using TiO_2 Degussa P25, whereas the substrate was only partially mineralized even after 14 h of irradiation in the presence of TiO_2 Merck. The final oxidation products were carbonate and nitrate. The appearance and the evolution of organic and inorganic intermediate species were also investigated and allowed to hypothesize the reaction pathways.

Keywords: Heterogeneous photocatalysis; Benzonitrile; Titanium dioxide

1. Introduction

Benzonitrile is a very toxic molecule extensively used as a solvent due to its high stability. Very few works concerning the benzonitrile abatement or its chemical modification are reported in the literature [1–3], although benzonitrile compounds are widely used as herbicides and fungicides and their fate in the environment is not completely known [4]. Anyway benzonitrile is a very interesting model molecule for photooxidation studies because it possesses an aryl and a nitrile group that may undergo different oxidation routes. Ehrich et al. [3] studied the direct oxidation of benzonitrile to its hydroxyderivates using N_2O as oxidant. The reaction was carried out in gas-solid regime on ZSM-5 type zeolites. They found mainly CO_2 but the three monohydroxybenzonitrile derivatives were also detected.

Heterogeneous photocatalysis is a technology successfully used to oxidise or reduce organic and inorganic species present both in vapour and in liquid effluents [5–8]. The photocatalytic process requires mild conditions and the degradation of recalcitrant, very toxic and non-biodegradable compounds is almost always achieved. TiO_2 is commonly used as photocatalyst due to its low cost, high activity and stability [9]. Photodegradation of *N*-containing compounds has been widely studied to investigate the relation between the inorganic species produced (in particular ammonium and nitrate ions) and the chemical structure of the starting molecule [10–13]. The heterogeneous photocatalytic degradation of benzonitrile at acid pH has been recently investigated [14]. Some papers have concerned the photodegradation of nitrile or amide functionalized molecules as acetonitrile [15–20], methanamide [10,13], ethanamide [21] and benzamide [22–24].

In this work, we report a study of the photocatalytic degradation of benzonitrile in the presence of TiO_2. The experiments were carried out at pH 11 in aqueous suspensions of two kinds of commercial polycrystalline TiO_2, i.e. Merck and Degussa P25, irradiated by ultraviolet light. The abatement of the substrate and of the total organic carbon (TOC) was monitored. The influence of the benzonitrile concentration on the photooxidation rate was investigated. Moreover, intermediate species and final degradation products were monitored throughout the photocatalytic experiments in order to study the fate of the nitrile group and of the aromatic ring.

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doi:10.1016/j.cattod.2007.06.045

2. Experimental

The study of the photocatalytic degradation of benzonitrile was carried out by using a discontinuous Pyrex batch photoreactor of cylindrical shape containing 1.5 L of aqueous suspension of TiO_2. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases, for sampling and for pH and temperature measurements. In selected runs, the outlet gas was bubbled in a trap containing an aqueous solution of NaOH at pH 12 to fix the hydrogen cyanide stripped from the reacting system and then in a trap containing an aqueous solution of HCl at pH 2 to fix the ammonia that could escape from the reactor. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture. A 500 W medium pressure Hg lamp (Helios Italquartz, Italy) was axially immersed within the photoreactor. The irradiance reaching the photoreactor (15.5 mW cm^{-2}) was measured in the 300–400 nm range by means of a radiometer UVX Digital leaned against the external wall of the photoreactor containing only pure water. The lamp was cooled by water circulating through a Pyrex thimble and the irradiated suspension had a temperature of about 300 K. Pure oxygen was continuously bubbled into the suspension for ca. 0.5 h before switching on the lamp and throughout the occurrence of the photoreactivity experiments. TiO_2 Merck (100% anatase, BET surface area: 10 $m^2\ g^{-1}$) and TiO_2 Degussa P25 (≈80% anatase, 20% rutile, BET surface area: 50 $m^2\ g^{-1}$) were used as the photocatalyts. For all of the runs the catalyst amount was 0.4 g L^{-1} and the initial pH of the suspension was adjusted to 11 by addition of NaOH. Initial benzonitrile concentrations were in the 0.14–0.77 mM range. All the reagents were analytical grade Fluka.

The photoreactivity runs lasted at least 5 h, but some selected runs lasted until 14 h. The analyses of the samples (5 ml volume) withdrawn from the suspensions at fixed intervals of time were performed after separation of the catalyst by filtration through 0.45 μm cellulose acetate membrane filters (HA, Millipore). A HPLC instrument constituted by a Varian 9012 Solvent Delivery System pump coupled with a Varian 9050 variable wavelength UV–vis detector was used to analyse benzonitrile and its organic degradation intermediates. A column Phenomenex Synergi 4 μm Fusion RP 80 (150 mm long × 2 mm i. d.) allowed an optimal separation of the peaks. A mixture of acetonitrile, water and an aqueous solution (80 mM) of KH_2PO_4 (42/30/28, v/v/v) was used as the eluant with a flow rate of 0.2 ml min^{-1}. The UV–vis detector was setted at 224 nm.

TOC analyses were carried out for all of the runs by using a 5000A Shimadzu total organic carbon analyser in order to follow the mineralization of the organics. The quantitative determination of the anions present in the reaction mixture during the runs was carried out by using an ionic chromatograph (Dionex DX 120) equipped with an ION PAC AS14A column (250 mm long × 4 mm i. d.). An aqueous solution of $NaHCO_3$ (2.8 mM) and Na_2CO_3 (2.2 mM) was used as eluant at the flow rate of 0.5 ml min^{-1}.

The concentrations of cyanide and ammonium ions were determined by means of selective electrodes connected to an Orion 720A+ analyser using calibration graphs of solutions of KCN and NH_4Cl as the authentic standards.

3. Results and discussion

Some preliminary experiments were carried out in order to investigate the adsorption of benzonitrile into the surface of the catalysts. The benzonitrile concentration was measured in liquid phase before and after the addition of the TiO_2 powders in dark conditions. The concentration values did not change significantly even after long times of contact under stirring indicating that benzonitrile scarcely adsorbs in the dark at pH 11 into both TiO_2 surfaces. Blank tests performed in the absence of catalyst but in the presence of UV light evidenced that no decrease of the substrate concentration occurred. The abatement of benzonitrile was observed only during the photocatalytic experiments. Fig. 1 shows the benzonitrile concentration versus irradiation time for runs carried out in the presence of the two TiO_2 samples.

Benzonitrile completely disappeared after 1–2 h, when TiO_2 Degussa P25 was used as the photocatalyst; whereas, its degradation was slower in the presence of TiO_2 Merck. The photocatalytic reaction followed a pseudo-first order kinetics under our experimental conditions.

The variation of the TOC concentration during two selected photodegradation runs is illustrated in Fig. 2. Benzonitrile was

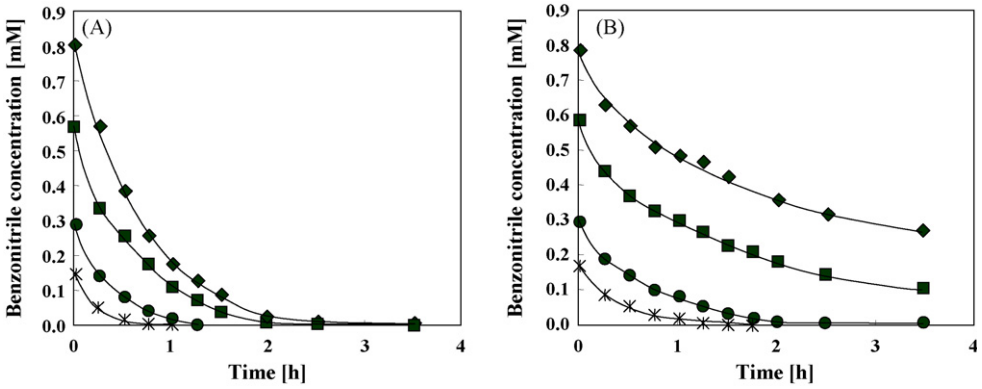

Fig. 1. Benzonitrile concentration vs. irradiation time for runs carried out in the presence of TiO_2 Degussa P25 (A) and TiO_2 Merck (B).

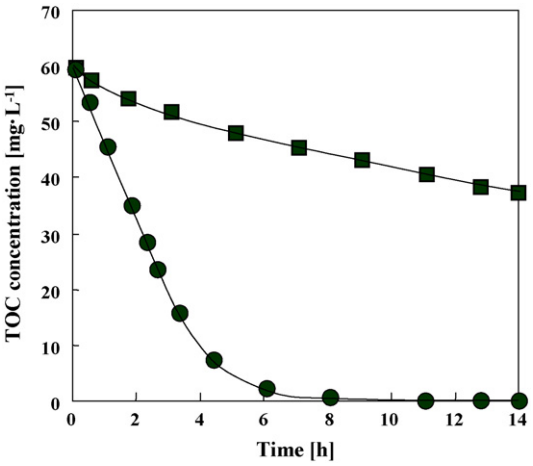

Fig. 2. TOC concentration vs. irradiation time for runs carried out in the presence of TiO_2 Degussa P25 (●) or TiO_2 Merck (■). Initial benzonitrile concentration equal to 0.70 mM.

completely mineralised after 8 h of irradiation in the presence of TiO_2 Degussa P25 but the percentage of degradation was only 35% by using TiO_2 Merck.

In order to compare the photoactivity of the two TiO_2 commercial samples, the initial reaction rate for benzonitrile disappearance (r_0) and the reaction rate values referred to the amount of photocatalyst surface area (r'_0), were calculated. The values of r_0 and r'_0 obtained in the presence of both photocatalysts versus the initial benzonitrile concentration are summarized in Fig. 3A and in Fig. 3B. Each figure is the mean value obtained from three different runs (the differences between the three values ranged between 1 and 4%) by applying a least-square best fitting procedure to the experimental data.

Degussa P25 exhibited the best performance if the initial reaction rates values are compared whereas TiO_2 Merck appears more active if r'_0 figures are considered. Anyway for both catalysts the initial reaction rate increased by increasing the benzonitrile concentration but it reached a plateau only when TiO_2 Merck was used. The plots observed in the presence of TiO_2 Merck follow a typical Langmuir pattern with an almost constant value of reaction rates for benzonitrile initial concentrations higher than 0.6 mM. This finding suggests the achievement of a complete coverage of the photoactive sites when the benzonitrile concentration exceeded 0.6 mM. On the contrary, the monotone increase of r_0 and r'_0 with the benzonitrile concentration observed in the presence of TiO_2 Degussa P25 indicates an incomplete coverage of the active sites by the molecules of benzonitrile even at the highest concentration used. The higher photoactivity of Degussa P25 could be due to its larger surface area, i.e. to a more significant number of global photoactive sites. This finding could justify the monotone increase of r_0 with the initial benzonitrile concentration only when P25 is used. On the other hand, the more significant activity per unit surface area exhibited by TiO_2 Merck could be attributed to a higher density and/or efficiency of the surface sites of this photocatalyst at least as far as the primary oxidant attack is concerned. A similar behaviour has been previously described for other substrates [17,25]. The inversion of the reactivity trend, as shown in Fig. 3A and B, suggests that the specific surface area cannot be used as the unique parameter to compare the photoefficiency of the photocatalysts.

As showed by the analytical techniques used in this work, benzonitrile degradation occurred via formation of various organic and inorganic intermediates. The same species were obtained by using both types of TiO_2 samples. The inorganic species found in significant amounts were cyanide, cyanate, nitrite, nitrate and ammonium ions, whereas the main organic intermediates were methanoate, mono- and di-hydroxybenzonitriles, 1,4-dihydroxybenzene, 1,2-dihydroxybenzene, benzoquinone, *trans*,*trans*-2,4-hexadienedioic acid, benzamide and methanamide. Traces of phenol were also detected.

The presence of these organic and inorganic species can be explained by the occurrence of different simultaneous photodegradation pathways as reported in Fig. 4.

Fig. 5 shows the evolution of the anionic intermediates formed during two photodegradation runs carried out by using TiO_2 Degussa P25 or TiO_2 Merck.

In the presence of TiO_2 Degussa P25, the cyanide ion concentration rapidly increased reaching a maximum value after 2.5 h of irradiation and soon after decreased, whereas with TiO_2 Merck the cyanide concentration still increased after 14 h of irradiation. A similar trend was observed for the methanoate concentration. Cyanate, nitrate and ammonium ions continuously increased during the runs. Small amounts of nitrite ions were also detected. It is worth nothing that the formation of all the intermediates proceeded more slowly by using TiO_2 Merck

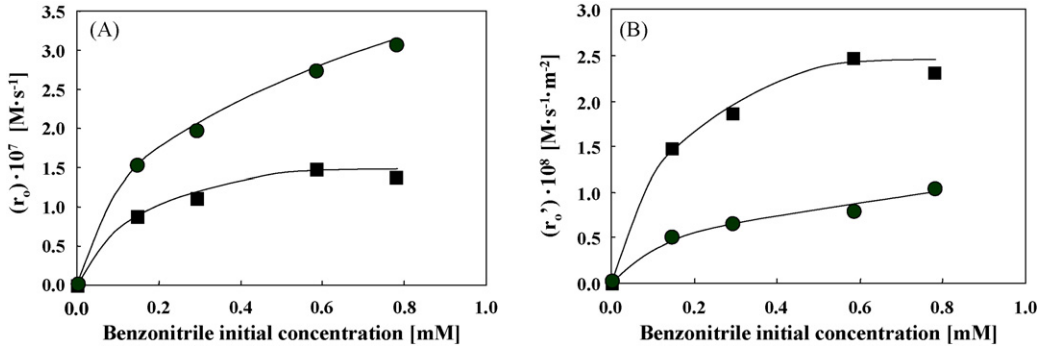

Fig. 3. Initial reaction rate (A) and initial reaction rate per unit of surface area (B) vs. initial benzonitrile concentration for runs carried out in the presence of Degussa P25 (●) and Merck (■).

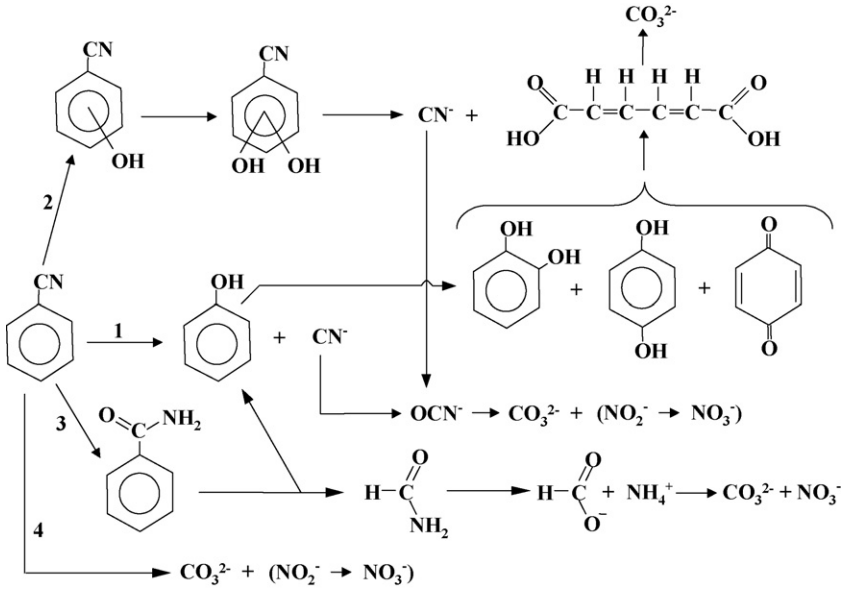

Fig. 4. Hypothesized benzonitrile photodegradation pathways.

even if the benzonitrile degradation rate per unit surface area was higher. This finding is related probably to a higher global surface photoactive sites number of TiO_2 Degussa P25.

The increase of the cyanide concentration from the early minutes of irradiation indicates the occurrence of the breakage of the carbon–carbon bond between the aromatic ring and the nitrile group (see pathway **1** in Fig. 4). Subsequently, as it has been previously reported [26–28], cyanide ions are oxidised to other intermediate species as cyanate and nitrite ions whereas nitrate, carbonate and hydrogen carbonate are obtained as final products.

The breakage of the C–C bond between an aliphatic radical and a nitrile group has been previously claimed to explain the mechanism of the photocatalytic degradation of acetonitrile both in gas–solid and in liquid–solid regimes [19], confirming that both aromatic and aliphatic nitriles give rise to this oxidation pathway. During the photocatalytic degradation of acetonitrile in gas phase the methyl moiety of the molecule is quickly oxidized to CO_2 and H_2O, whereas the inorganic part of the substrate forms hydrogen cyanide. Zhuang et al. [18] evidenced the presence of isocyanate ions that were oxidized to CO_2 and N_2 by lattice oxygen of TiO_2. In liquid–solid regime acetonitrile gives rise to cyanide and methanoate ions that eventually mineralise to carbonate.

In the case of benzonitrile degradation, after the C–C bond breakage and the formation of cyanide and phenol, the aromatic part of the molecule is subjected to other further oxidation steps (see pathway **1** in Fig. 4). Indeed 1,2-dihydroxybenzene, 1,4-dihydroxybenzene and benzoquinone were obtained, although in very small amounts, since the first minutes of reaction. These aromatic compounds are well known intermediates of the phenol photocatalytic oxidation [29–32]. In the literature it is reported moreover that the fate of these aromatic species is their transformation to *trans*,*trans*-2,4-hexadienedioic acid that was also observed throughout the photocatalytic runs.

Contemporaneously to the formation of the previous organic species, the presence of mono- and dihydroxybenzonitriles suggests a parallel oxidation pathway consisting in the hydroxylation of the benzonitrile molecule (see pathway **2** in

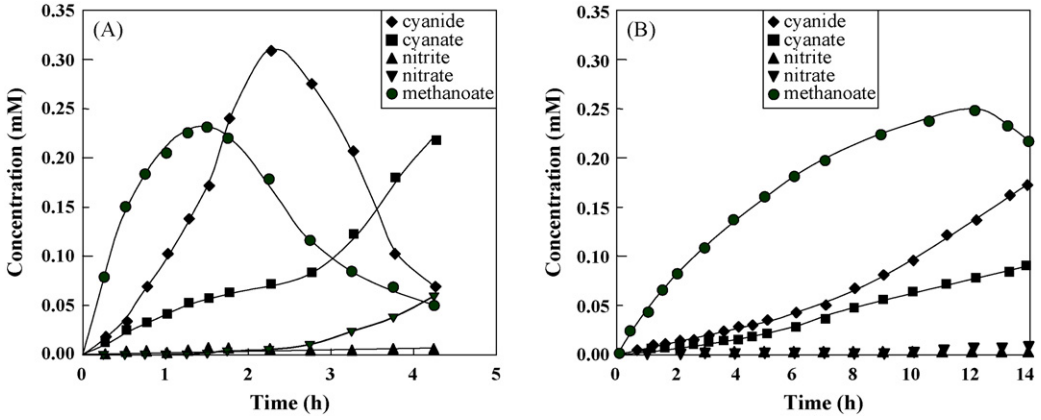

Fig. 5. Evolution of the anionic intermediate and product species vs. irradiation time for runs carried out in the presence of TiO_2 Degussa P25 (A) or TiO_2 Merck (B). Initial benzonitrile concentration equal to 0.70 mM.

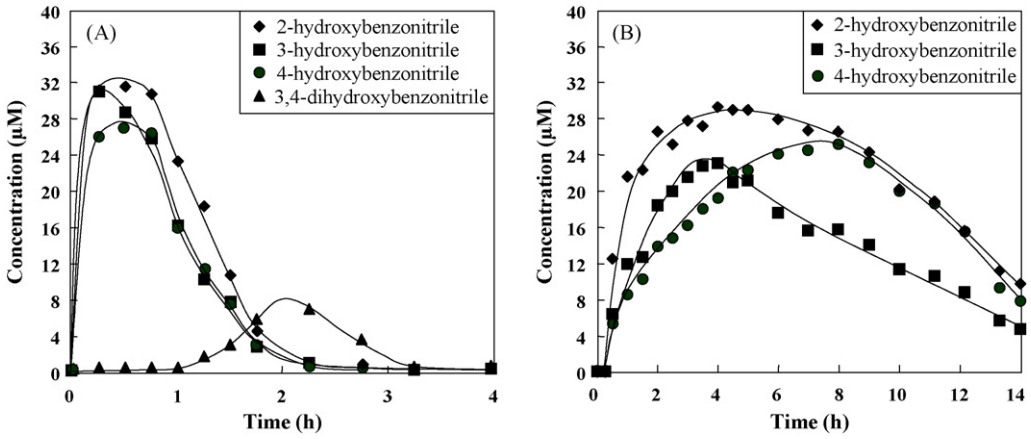

Fig. 6. Evolution of mono- and di-hydroxybenzonitriles species vs. irradiation time for runs carried out in the presence of TiO_2 Degussa P25 (A) and TiO_2 Merck (B). Initial benzonitrile concentration equal to 0.70 mM.

Fig. 4). Fig. 6 shows the evolution of hydroxybenzonitrile intermediates obtained during the photocatalytic oxidation of benzonitrile in the presence of both photocatalysts. The concentration of all these aromatic species increased with irradiation time reaching a maximum and then decreased for further irradiation. These species disappeared after ca. 3 h. of irradiation in the presence of TiO_2 Degussa P25, while monohydroxybenzonitriles were found even after long irradiation times (14 h) by using TiO_2 Merck. In any case, it is worth noting that the maximum amount of these intermediate species was one order of magnitude smaller than the initial benzonitrile concentration.

The presence of a small amount of benzamide from the start of irradiation (not reported in Fig. 6 for the sake of clarity) suggests a third reaction pathway according to which the nitrile group present in the benzonitrile molecule is hydrolysed giving rise to an amide group (see pathway **3** in Fig. 4). Pichat and co-workers [22] studied the benzamide photocatalytic degradation and described not only the appearance of hydroxylated benzamide derivates but also the subsequent formation of 1,2-dihydroxybenzene and 1,4-dihydroxybenzene. Moreover, methanamide was also detected and its presence can be explained by considering the breakage of the C–C bond between the amide group and the aromatic ring. Methanamide was then hydrolysed to ammonium and methanoate ions that were also found in the solution. These results are in accord with those reported by Hidaka and co-workers [11] and by Pelizzetti et al. [13] who obtained ammonium from the photocatalytic degradation of methanamide.

By comparing the slopes of the benzonitrile disappearance plot at zero time (Fig. 1) with the slopes of the plots relative to the production of intermediates (Fig. 5), it is evident that the first values are quite higher than the sum of the last ones. This finding derives from the fact that one of the main oxidation products, CO_2, arises from a further pathway in parallel with the previous ones (see pathway **4** in Fig. 4). An experimental evidence of the occurrence of this process derives from the observation that the TOC decreases from the starting of irradiation (see Fig. 2). It is obvious that the evolution to CO_2 is not a single step process, but it occurs through various oxidation steps involving unknown intermediate species that are strongly adsorbed onto the irradiated TiO_2 surface without being released into the bulk of the solution.

4. Conclusions

The results reported in this paper show that the heterogeneous photocatalytic method could be successfully used for the complete degradation of benzonitrile in aqueous basic solution by using suspended polycrystalline TiO_2.

The evolution of the organic and inorganic species found throughout the photoreactivity runs suggests the occurrence of various parallel pathways, for both catalysts used: (i) breakage of the carbon–carbon bond between the aromatic ring and the nitrile group that gives rise to the formation of cyanide anions and phenols released into the bulk of the solution and successively mineralised; (ii) formation of monohydroxybenzonitrile species released into the bulk of the solution, successively transformed into dihydroxylated compounds, aliphatic species and eventually into CO_2; (iii) formation of benzamide released also into the bulk of the solution and then completely degraded (at least in the presence of TiO_2 Degussa P25) to CO_2, ammonium and nitrate ions; (iv) photodegradation of strongly adsorbed species with final production of CO_2.

Acknowledgement

The authors wish to thank MIUR (Rome) for financial support.

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