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## Ozone Formation from Illuminated Titanium Dioxide Surfaces

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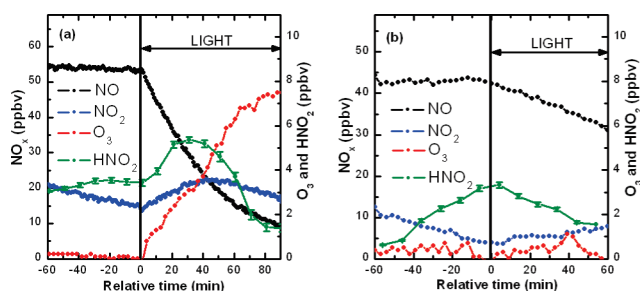
Titanium dioxide, TiO<sub>2</sub>, is used in a variety of remediation processes due to its favorable physical, chemical, and photocatalytic properties.<sup>1–3</sup> Possible removal of NO<sub>x</sub> by means of depolluting surfaces containing TiO<sub>2</sub> has been previously reported.<sup>4–13</sup> Other recent studies<sup>14–17</sup> show that this process converts NO<sub>2</sub> to HNO<sub>2</sub> producing also H<sub>2</sub>O<sub>2</sub><sup>18</sup> and nitrate anions<sup>9,18–22</sup> which are then involved in a renoxification process.<sup>23</sup> Similarly, the photochemistry of adsorbed nitrate on aluminum oxide has been proven to produce NO, NO<sub>2</sub>, and N<sub>2</sub>O.<sup>24,25</sup> However, the formation of non-nitrogen containing products in the NO<sub>x</sub> reaction with illuminated TiO<sub>2</sub> surfaces has been largely unexplored.

Herein, we report the first investigation of such products from TiO<sub>2</sub> coated glasses exposed to nitrogen oxides (NO<sub>x</sub>) in two simulation chambers using both artificial and natural illumination and from irradiated TiO<sub>2</sub>/KNO<sub>3</sub> films using a coated-wall flow tube reactor. These studies demonstrate the formation of ozone from TiO<sub>2</sub> surfaces containing nitrate anions.

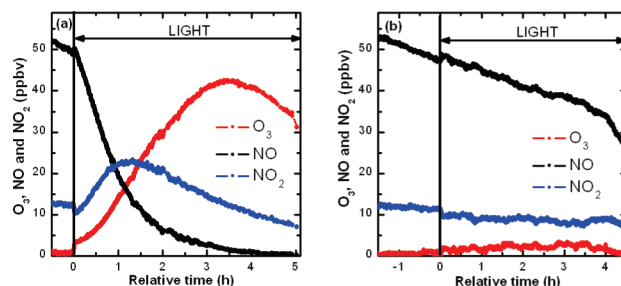
Chamber simulation experiments are performed in two different chambers (i) a stainless steel Multiphase Atmospheric Experimental Simulation Chamber (CESAM) equipped with artificial irradiation and (ii) a Teflon outdoor chamber (see Supporting Information for experimental details and Figures S1–S3). After introduction of synthetic air and NO into the CESAM chamber, the concentrations of NO, NO<sub>2</sub>, HNO<sub>2</sub>, and O<sub>3</sub> are monitored in the dark for 1 h. Then, the artificial illumination is turned on, and the gas mixture is again monitored for typically 90 min.

A similar procedure is adopted for the experiments conducted in the Teflon outdoor chamber using natural illumination. In the latter, known amounts of NO and NO<sub>2</sub> are injected after flushing with dry purified air, and the NO, NO<sub>2</sub>, and O<sub>3</sub> concentrations are monitored for 30 min in the dark. The reactor is then exposed to natural light, and the gas mixture composition is monitored for 4 h. The results for a TiO<sub>2</sub> coated glass and for a standard glass studied with the CESAM and the outdoor chamber are displayed in Figures 1 and 2, respectively. An example of the NO, NO<sub>2</sub>, and O<sub>3</sub> concentration–time profiles obtained in the absence of any surface using the outdoor chamber is shown in Figure S4.

Despite the different time scales and the chamber characteristics (i.e., irradiation type and chambers building material) the observed trace gas evolution is similar over a TiO<sub>2</sub> coated glass. In agreement with previous studies,<sup>26</sup> NO uptake on the TiO<sub>2</sub> coated glass is enhanced under irradiation increasing with time in both experiments. The NO<sub>2</sub> concentration profile exhibits a maximum under illumina-



**Figure 1.** NO, NO<sub>2</sub>, HNO<sub>2</sub>, and O<sub>3</sub> concentration profiles over (a) a TiO<sub>2</sub> coated glass and (b) a standard glass (TiO<sub>2</sub> free) in the CESAM chamber. The vertical line indicates the start of the irradiation.



**Figure 2.** NO, NO<sub>2</sub>, and O<sub>3</sub> profiles under natural irradiation in the presence of (a) a TiO<sub>2</sub> coated glass and (b) a standard glass in the outdoor chamber. The vertical line indicates the start of the irradiation.

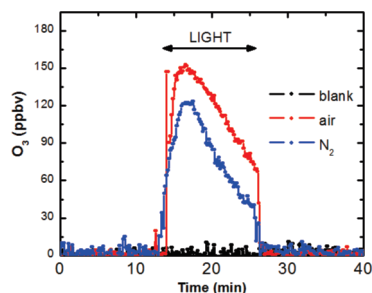
tion, suggesting that it is formed from NO photocatalytic oxidation and then converted into HNO<sub>3</sub> and HNO<sub>2</sub> at the surface.<sup>14–17,22</sup> At the same time, a significant accumulation of ozone is observed. In agreement with previous studies,<sup>14–16</sup> HNO<sub>2</sub> production is enhanced under irradiation in the presence of TiO<sub>2</sub> (Figure 1). However, when a standard glass (i.e., TiO<sub>2</sub> free) is analyzed in both chambers, no O<sub>3</sub> formation is observed (Figures 1b and 2b). The NO<sub>2</sub> and NO concentration–time profiles obtained in the absence of glass samples are similar to those observed in the presence of standard glasses, with no evidence of any light effect (Figures 2b and S4). These results clearly suggest that O<sub>3</sub> formation cannot be explained by the gas phase chemistry occurring in the chambers. The differences between the O<sub>3</sub> profiles from the blank experiments and the coated glass indicate that TiO<sub>2</sub> should be involved in the reaction mechanism leading to O<sub>3</sub> formation probably via new surface reactions.

To further investigate the reason for O<sub>3</sub> production, a second type of experiment has been carried out using a flow tube reactor, where only air or N<sub>2</sub> was present in the gas phase. It is well-known

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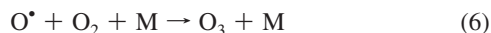
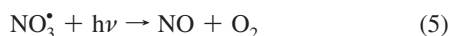
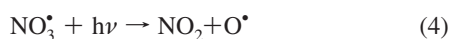
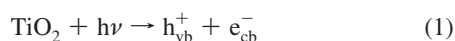
<sup>§</sup> ICARE.



**Figure 3.** Effect of light (8 near-UV emitting lamps in the 300–420 nm wavelength range) on a  $\text{TiO}_2/\text{KNO}_3$  (50% w/w) film using synthetic air and pure  $\text{N}_2$  as carriers. The same blank signal was given by an empty tube and by a tube with a  $\text{KNO}_3$  deposit using both carriers.

that nitrate anions are formed as a consequence of the photocatalytic oxidation of  $\text{NO}_2$  on UV-illuminated  $\text{TiO}_2$  surfaces.<sup>9,18–22</sup> Therefore a film of  $\text{TiO}_2/\text{KNO}_3$  50% w/w has been exposed to near-UV irradiation (300–420 nm) using synthetic air or pure  $\text{N}_2$  as a carrier gas with 30% RH under atmospheric pressure and at  $T = 298 \pm 1$  K (Figure 3).

As described previously, a renoxification process occurs on illuminated  $\text{TiO}_2$  films mixed with nitrate.<sup>23</sup> In contrast with the mechanism proposed by Grassian and co-workers<sup>24,25</sup> for the photochemistry of adsorbed nitrate on alumina, control experiments indicate that nitrate photolysis is negligible under the experimental conditions (Figure 3).  $\text{NO}_3^-$  reduction by conduction band electrons may lead to the release of  $\text{NO}_x$ , but it does not explain  $\text{O}_3$  formation.<sup>27</sup> An alternative surface chemical pathway would involve the photochemistry of the  $\text{NO}_3$  radical, produced by a charge exchange reaction between the nitrate anion and the solid surface, followed by photolysis of the radical (occurring at longer wavelength compared to the anion)<sup>23</sup> according to



$\text{TiO}_2$  band gap excitation (eq 1) produces excited-state conduction-band electrons and valence-band holes, which can then react with electron acceptors and electron donors adsorbed onto the semiconductor surface. According to Marcus theory,<sup>28</sup> the activation energy ( $\Delta G^\ddagger$ ) for the oxidation of nitrate anion into nitrate radical by the holes can be calculated by eq 8:

$$\Delta G^\ddagger = \frac{\lambda}{4} \left( 1 - \frac{F(E_{\text{vb}} - E_{\text{NO}_3^{\bullet}/\text{NO}_3^-})}{\lambda} \right)^2 \quad (7)$$

where  $\lambda$  is the reorganization energy necessary to transform the nuclear configurations in the reactant and the solvent to those on the product state;  $E_{\text{vb}} = 3.25\text{--}0.06\text{ pH V}$  (vs NHE) is the valence band edge potential<sup>29</sup> in  $\text{TiO}_2$  and  $E = 2.3\text{--}2.5$  V (vs NHE) is the redox potential range for the  $\text{NO}_3^{\bullet}/\text{NO}_3^-$  couple.<sup>30,31</sup> Assuming that the reorganization energy accounts for only the solvent contribution and that it is approximately 0.5 eV,<sup>29</sup> then  $\Delta G^\ddagger$  approaches zero, so  $h_{\text{vb}}^+$  can directly oxidize  $\text{NO}_3^-$ .

New surface reactions occurring on illuminated  $\text{TiO}_2$  surfaces are discussed, for the first time, as a possible source of  $\text{O}_3$ . Although  $\text{O}_3$  has been recently proven to decompose on illuminated  $\text{TiO}_2$  surfaces,<sup>32</sup> its formation is observed when  $\text{TiO}_2$  treated surfaces are exposed to  $\text{NO}_x$  under illumination. Charge transfer reactions are taking place at the surface of  $\text{TiO}_2$ , producing nitrate radicals from the corresponding anions. The photochemistry of the  $\text{NO}_3$  radical leads to  $\text{O}_3$  formation, enhancing the oxidizing power of these surfaces.

**Acknowledgment.** We acknowledge the French Ministry for Environment and Ademe for support from the Primequal2 grant PhotoBat and the ANR for support from the NeoRad grant. This work was also supported by the European Community within the 7th Framework Program, through the EUROCHAMP-2 project.

**Supporting Information Available:** Experimental procedures, Figures S1–S4, and references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA1018755