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Ozone Formation from Illuminated Titanium Dioxide Surfaces

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Titanium dioxide, TiO_2, is used in a variety of remediation processes due to its favorable physical, chemical, and photocatalytic properties.[1–3] Possible removal of NO_x by means of depolluting surfaces containing TiO_2 has been previously reported.[4–13] Other recent studies[14–17] show that this process converts NO_2 to HNO_2 producing also H_2O_2[18] and nitrate anions[9,18–22] which are then involved in a renoxification process.[23] Similarly, the photochemistry of adsorbed nitrate on aluminum oxide has been proven to produce NO, NO_2, and N_2O.[24,25] However, the formation of non-nitrogen containing products in the NO_x reaction with illuminated TiO_2 surfaces has been largely unexplored.

Herein, we report the first investigation of such products from TiO_2 coated glasses exposed to nitrogen oxides (NO_x) in two simulation chambers using both artificial and natural illumination and from irradiated TiO_2/KNO_3 films using a coated-wall flow tube reactor. These studies demonstrate the formation of ozone from TiO_2 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_2, HNO_2, and O_3 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_2 are injected after flushing with dry purified air, and the NO, NO_2, and O_3 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_2 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_2, and O_3 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_2 coated glass. In agreement with previous studies,[26] NO uptake on the TiO_2 coated glass is enhanced under irradiation increasing with time in both experiments. The NO_2 concentration profile exhibits a maximum under illumination, suggesting that it is formed from NO photocatalytic oxidation and then converted into HNO_3 and HNO_2 at the surface.[14–17,22] At the same time, a significant accumulation of ozone is observed. In agreement with previous studies,[14–16] HNO_2 production is enhanced under irradiation in the presence of TiO_2 (Figure 1). However, when a standard glass (i.e., TiO_2 free) is analyzed in both chambers, no O_3 formation is observed (Figures 1b and 2b). The NO_2 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_3 formation cannot be explained by the gas phase chemistry occurring in the chambers. The differences between the O_3 profiles from the blank experiments and the coated glass indicate that TiO_2 should be involved in the reaction mechanism leading to O_3 formation probably via new surface reactions.

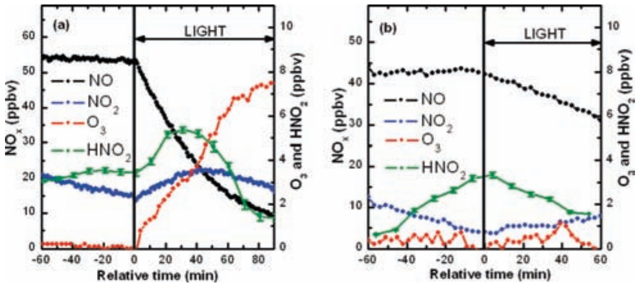

Figure 1. NO, NO_2, HNO_2, and O_3 concentration profiles over (a) a TiO_2 coated glass and (b) a standard glass (TiO_2 free) in the CESAM chamber. The vertical line indicates the start of the irradiation.

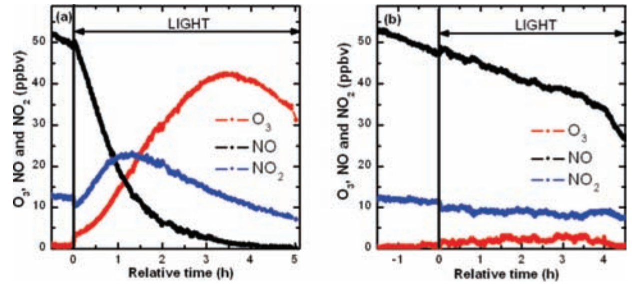

Figure 2. NO, NO_2, and O_3 profiles under natural irradiation in the presence of (a) a TiO_2 coated glass and (b) a standard glass in the outdoor chamber. The vertical line indicates the start of the irradiation.

To further investigate the reason for O_3 production, a second type of experiment has been carried out using a flow tube reactor, where only air or N_2 was present in the gas phase. It is well-known

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10.1021/ja1018755

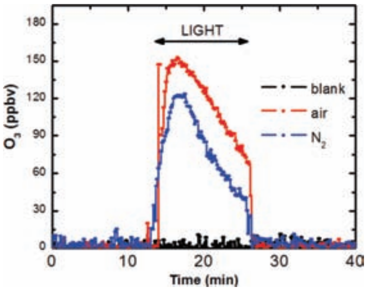

Figure 3. Effect of light (8 near-UV emitting lamps in the 300−420 nm wavelength range) on a TiO_2/KNO_3 (50% w/w) film using synthetic air and pure N_2 as carriers. The same blank signal was given by an empty tube and by a tube with a KNO_3 deposit using both carriers.

that nitrate anions are formed as a consequence of the photocatalytic oxidation of NO_2 on UV-illuminated TiO_2 surfaces.[9,18–22] Therefore a film of TiO_2/KNO_3 50% w/w has been exposed to near-UV irradiation (300−420 nm) using synthetic air or pure 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 TiO_2 films mixed with nitrate.[23] In contrast with the mechanism proposed by Grassian and co-workers[24,25] for the photochemistry of adsorbed nitrate on alumina, control experiments indicate that nitrate photolysis is negligible under the experimental conditions (Figure 3). NO_3^- reduction by conduction band electrons may lead to the release of NO_x, but it does not explain O_3 formation.[27] An alternative surface chemical pathway would involve the photochemistry of the 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)[23] according to

$$TiO_2 + h\nu \rightarrow h^+_{vb} + e^-_{cb} \tag{1}$$

$$O_2 + e^-_{cb} \rightarrow O_2^{\bullet -} \tag{2}$$

$$NO_3^- + h^+_{vb} \rightarrow NO_3^{\bullet} \tag{3}$$

$$NO_3^{\bullet} + h\nu \rightarrow NO_2 + O^{\bullet} \tag{4}$$

$$NO_3^{\bullet} + h\nu \rightarrow NO + O_2 \tag{5}$$

$$O^{\bullet} + O_2 + M \rightarrow O_3 + M \tag{6}$$

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,[28] the activation energy ($\Delta G^{\neq}$) for the oxidation of nitrate anion into nitrate radical by the holes can be calculated by eq 8:

$$\Delta G^{\neq} = \frac{\lambda}{4}\left(1 - \frac{F(E_{vb} - E_{NO_3^{\bullet}/NO_3^{-}})}{\lambda}\right)^2 \tag{7}$$

where λ is the reorganization energy necessary to transform the nuclear configurations in the reactant and the solvent to those on the product state; $E_{vb} = 3.25-0.06$pH V (vs NHE) is the valence band edge potential[29] in TiO_2 and $E = 2.3-2.5$ V (vs NHE) is the redox potential range for the $NO_3^{\bullet}/NO_3^-$ couple.[30,31] Assuming that the reorganization energy accounts for only the solvent contribution and that it is approximately 0.5 eV,[29] then $\Delta G^{\neq}$ approaches zero, so h^+_{vb} can directly oxidize NO_3^-.

New surface reactions occurring on illuminated TiO_2 surfaces are discussed, for the first time, as a possible source of O_3. Although O_3 has been recently proven to decompose on illuminated TiO_2 surfaces,[32] its formation is observed when TiO_2 treated surfaces are exposed to NO_x under illumination. Charge transfer reactions are taking place at the surface of TiO_2, producing nitrate radicals from the corresponding anions. The photochemistry of the NO_3 radical leads to 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