

Spontaneous and Light-Driven Conversion of NO_x on Oxide-Modified TiO₂ Surfaces

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ABSTRACT: Heterogeneous reactions of trace atmospheric gases on solid surfaces play an important role in atmospheric chemistry. In this study, we investigate the reaction of NO₂ with solid surfaces of TiO₂ covered with a thin layer of an alumina–silica mixture over a range of different compositions. The reactions were conducted in the presence of oxygen under dark or ultraviolet light (UV) illumination conditions. The results show that coating TiO₂ with alumina–silica greatly affects the formation of gas-phase products NO and N₂O both with or without illumination using UV light. A thick shell of alumina–silica enhances the formation of NO in the dark, whereas adding a small amount of alumina on the surface of rutile TiO₂ significantly enhances the conversion of NO₂ to NO under UV illumination. Overall rates of conversion (on the order of mg/m² paint/year) suggest that these materials should have negligible impact on NO_x levels in the environment.

1. INTRODUCTION

Nitrogen oxides (NO_x) are common pollutants that are major causes of acid rain, photochemical smog, and depletion of the ozone layer. In addition, they are also strongly correlated with adverse human health effects.¹ In the atmosphere, nitrogen oxides can readily react with particulate matter (e.g., mineral dust) which may result in changes in gas-phase chemical composition as well as changes occurring at surfaces. This process strongly affects the concentration of ozone which is formed by a complex series of nonlinear reactions involving NO_x and volatile organic compounds.^{2,3} Understanding the chemical and photochemical reactions of NO_x on the surface of mineral oxides is therefore of considerable importance.

Over the past decades, heterogeneous reactions involving NO_x on the surface of various earth-abundant oxides such as Al₂O₃, Fe₂O₃, TiO₂, and SiO₂ have been studied extensively.^{2,4–7} For example, the interaction of NO₂ with Al₂O₃ surfaces was found to lead to the formation of various nitrogen-containing species on the alumina surface, including nitrite and nitrate and, in the gas phase, NO and N₂O.^{8–10} On Fe₂O₃ surfaces, NO₂ can interact with adsorbed water to form adsorbed nitrate species. Irradiation of adsorbed nitrate on Fe₂O₃ with UV light generates three nitrogen gas-phase products including NO₂, NO, and N₂O.⁷ The formation of adsorbed nitrate and gaseous NO has also been observed when NO₂ interacts with a Cr₂O₃ surface in the presence of moisture, oxygen, and UV illumination.⁶

Among various metal oxides, the reaction of NO₂ on the surface of TiO₂ in the dark and under UV illumination has received particular interest because TiO₂ is used as white pigment in paint, plastic, and paper. Its advantages include a very high refractive index, insolubility, and nontoxicity.¹¹ In addition, TiO₂ exhibits promise as a photocatalyst for a variety of remediation processes because of its good photocatalytic activity and high chemical and photochemical stability.¹² In particular, TiO₂ has been demonstrated to enhance the oxidation of NO_x to nitrate under UV illumination.^{13–16} On the surface of TiO₂, adsorbed NO_x species can undergo several chemical reactions in the dark and under UV illumination that

produce different nitrogen-containing products. The heterogeneous reaction between NO₂ and TiO₂ was found to yield adsorbed nitrate and gas-phase NO.¹⁷ It has also been found that UV-activated TiO₂ photocatalyzes the conversion of NO₂ and water to nitrous acid with high efficiency.^{18,19} In the case of an TiO₂–SiO₂ mixture, NO, nitrous acid, and nitrate were the products when NO₂ interacted with the metal oxide surfaces under UV illumination.²⁰

Although the reactions of NO₂ on the surface of pure TiO₂ and on TiO₂-based mixed oxides have been the subject of several studies,^{17–25} information about the reactivity of TiO₂ coated with a thin layer of other oxides on this reaction is limited. The topic is nevertheless of considerable practical importance, since coating TiO₂ with a thin layer of oxide such as alumina or silica is widely practiced in the paint industry to decrease photocatalytic activity. This coating layer makes paints more stable by slowing the degradation of organic components that would otherwise arise due to the photoactivity of TiO₂. However, this surface modification of TiO₂ is also expected to change the surface chemistry of TiO₂ toward NO_x molecules. With an annual consumption of an estimated 30 billion liters of paint, corresponding to an amount of 10.8 billion kilograms of TiO₂, the reactivity of surface-modified TiO₂ toward atmospheric gases may reasonably be expected to have a significant effect on the natural environment.

In this study, we therefore investigate the reaction of NO₂ with solid surfaces of TiO₂ covered with a thin layer of Al₂O₃ and SiO₂. We studied this under dark conditions and in the presence of UV light. We find that coating TiO₂ with Al₂O₃ and SiO₂ greatly increases the conversion of NO₂ to NO on TiO₂ in dark conditions. The reactivity of TiO₂ was also found to be dependent on the composition of the coated shell. Moreover, adding a small amount of alumina to the rutile TiO₂ surface

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significantly increases the formation of NO under UV illumination.

2. EXPERIMENTAL SECTION

Materials. Rutile TiO₂ samples (P1, P2, P3, and P4) were provided by DuPont. P1 sample is rutile TiO₂ with 1.7 wt % of alumina. P2 through P4 are rutile TiO₂ coated with alumina–silica mixture with different compositions as detailed in Table 1. Anatase A1 sample was purchased from Crystal Corporation.

Table 1. Textural Properties and Chemical Composition of the Samples

sample	particle size (nm)	crystalline phase	specific surface area (m ² /g)	chemical composition (wt %)		surface atomic ratio Ti:Al:Si
				Al ₂ O ₃	SiO ₂	
P1	200–300	rutile	7.3	1.7	0	1:0.6:0
P2	200–300	rutile	12.1	2.5	3.5	1:4.5:4.6
P3	200–300	rutile	15.3	4.3	1.4	1:6.3:1.8
P4	200–300	rutile	13.6	3.5	6.5	1:8.5:9
A1	<10	anatase	320	0	0	1:0:0

Material Characterization. The morphology of each sample was characterized via scanning electron microscopy (SEM, FEI Quanta FEG 250) with an acceleration voltage of 5 kV. High resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL 2010 instrument operated at 200 kV. Powder X-ray diffraction (XRD) patterns of the samples were obtained using a Bruker SMART APEXII X-ray diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$). The UV–visible (UV–vis) absorbance spectra were recorded using PerkinElmer 950 UV–vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ion-pumped chamber (evacuated to 10^{−9} Torr) of a photoelectron

spectrometer (PHI-5500) equipped with a focused X-ray source (Al K α , $h\nu = 1486.7 \text{ eV}$). The binding energy scale was calibrated using the Au 4f_{7/2} peak at 83.98 eV and the Cu 2p_{3/2} peak of sputter-cleaned Cu at 932.67 eV.

Photocatalytic Setup. The conversion of NO₂ with solid TiO₂ films was studied at ambient pressure using a flow reactor with a long path length FTIR detector. The reactor was made of aluminum equipped with a square quartz window with an area of 15 × 15 cm². Typically, 5 g of catalyst was coated on glass substrate (15 × 15 cm²) to make the TiO₂ film. The catalyst was first mixed with ethanol (5 mL), and the mixture was sonicated for 1 h before it was uniformly coated on a glass substrate. The obtained catalyst film was dried at room temperature overnight and was then heated to 200 °C in an oven for 5 h to remove surface impurities. NO₂ (100 ppm) in dried air and pure dried air (Linde, HiQ Certificate) were used as gas sources. A flow of NO₂ in air (20 mL/min) was mixed with a flow of pure air (180 mL/min) to produce a flow (200 mL/min) containing 10 ppm of NO₂ as reaction gas. Before the reaction, the reactor chamber containing the catalyst film was heated to 100 °C under a flow of dried air (200 mL/min) for 5 h to remove the adsorbed impurities. Products in the gas phase coming out of the reactor were monitored using the IR instrument (Bruker) equipped with the long path length gas detector (path length of 10 m), which enabled a detection limit of 10 ppb. A UV lamp generating 254 nm light with an intensity of 16 W/m² was used as the light source. UV light with wavelength of 254 nm was chosen to limit the effect of NO_x photolysis under UV illumination.²⁶

To analyze the products quantitatively, we obtained calibration curves for NO, NO₂, and N₂O using standard NO, NO₂, and N₂O gases diluted in nitrogen. Calibration concentrations were adjusted from 10 ppb to 10 ppm. The detection and analysis of NO₂ was based on the IR band in the region of 1584–1605 cm^{−1}. For NO gas, the band in the range of 1800–1950 cm^{−1} was chosen. The band for N₂O is in the range of 2175–2260 cm^{−1}.²¹

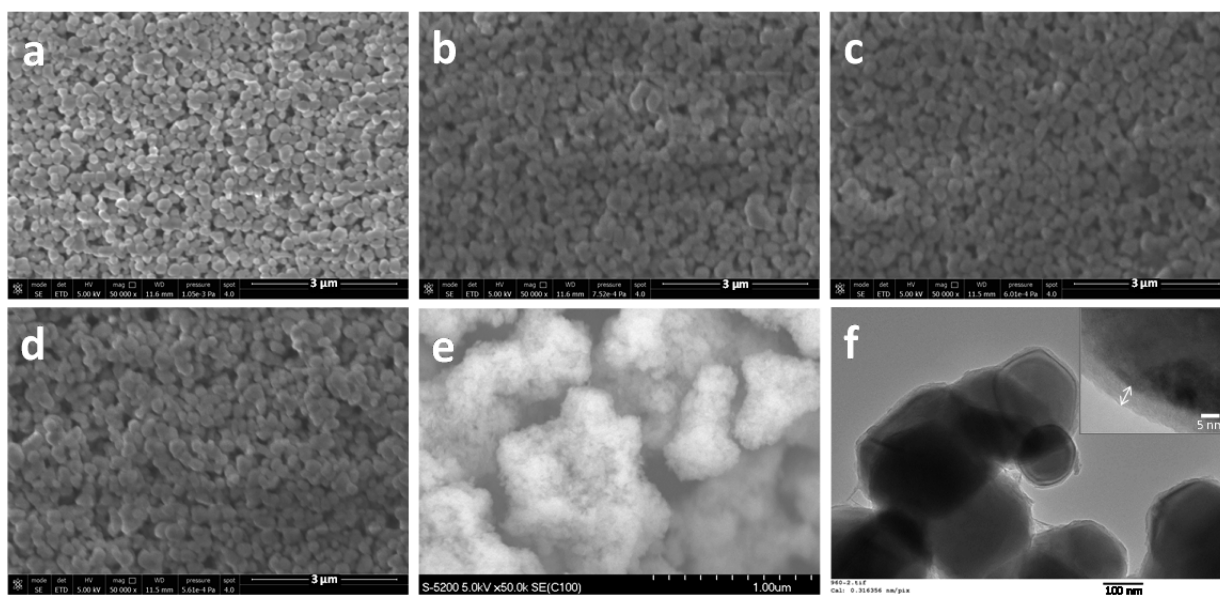


Figure 1. SEM images of P1 (a), P2 (b), P3 (c), P4 (d), and A1 (e) and HRTEM image of P4 (f). Arrow in (f) shows the thickness of the coating layer.

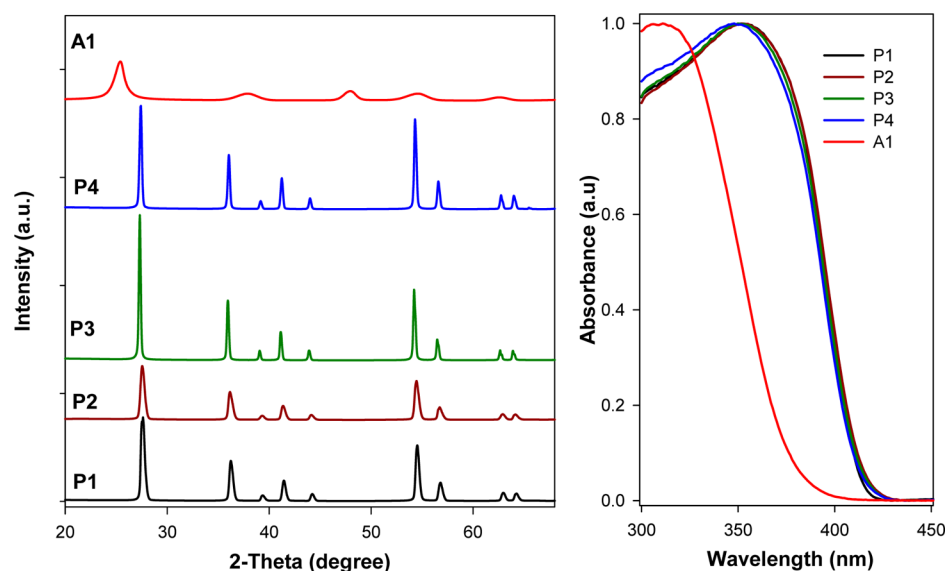


Figure 2. XRD patterns (left) and UV-vis spectra (right) of the samples.

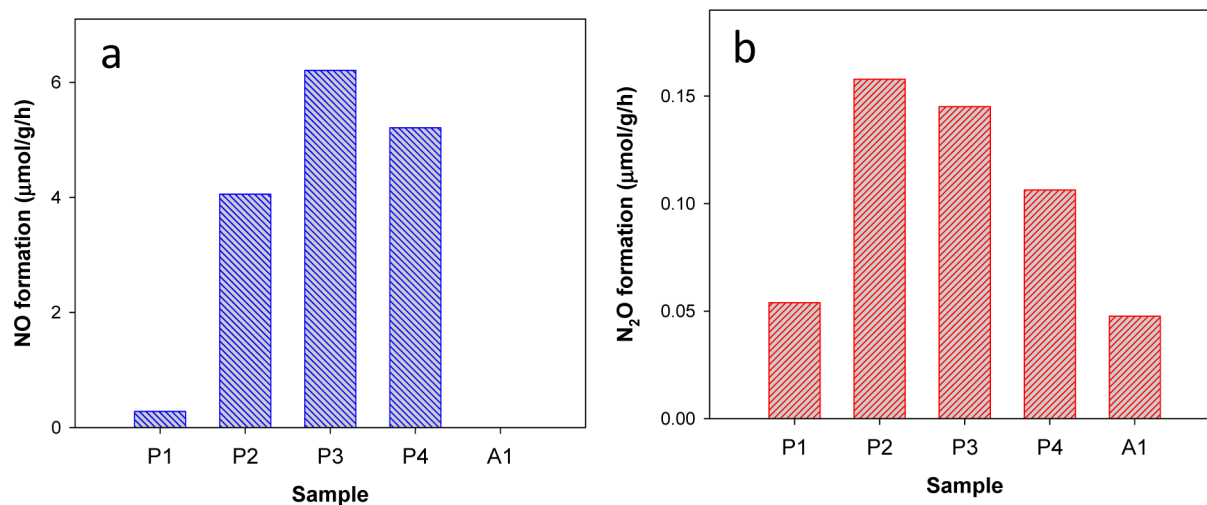


Figure 3. Formation rates of NO (a) and N₂O (b) of the conversion of NO₂ over different catalysts in the dark condition.

3. RESULTS AND DISCUSSION

Material Characterization. Figure 1a–e shows scanning electron microscopy (SEM) images of the catalysts. P1–P4 samples exhibit a round shape with particle size in the range of 200–300 nm. Compared to the pigmentary samples, the A1 anatase TiO₂ particles are smaller with an average particle size of 5–10 nm. To confirm the core–shell structure of the coated sample, we used high-resolution transmission electron microscopy (HRTEM): Figure 1f shows HRTEM images of a representative coated TiO₂ sample P4. All particles appear homogeneously encapsulated by amorphous layers. The thickness of the coated layer is between 5 and 10 nm (inset in Figure 1f).

The powder X-ray diffraction patterns of the P1, P2, P3, and P4 samples (Figure 2) exhibit well-defined and intense peaks that are assigned to the pure rutile phase with high crystallinity. No characteristic peaks of crystalline alumina were observed on the coated samples (P2, P3, and P4), indicating the amorphous nature of coated shell. In contrast, the XRD pattern of A1 samples shows diffraction peaks that are characteristic of pure TiO₂ anatase phase. Compared to the diffraction peaks of rutile

samples, the diffraction peaks in anatase TiO₂ A1 are broader, indicating the smaller size of anatase particles, in good agreement with SEM.

The optical properties of the samples were characterized via ultraviolet–visible absorption spectroscopy (UV-vis). As shown in Figure 2, the UV-vis spectra of P1, P2, P3, and P4 samples show a typical absorption edge at around 410 nm, corresponding to a bandgap of 3.0 eV, which is characteristic of rutile TiO₂. In addition, the UV-vis spectra of these samples are indistinguishable, suggesting that coating TiO₂ with a thin layer of alumina–silica does not change its optical properties. In the case of the A1 sample, the UV-vis spectrum shows an absorption edge at 380 nm, corresponding to a bandgap of 3.2 eV of anatase TiO₂.

The chemical states and surface composition of the samples were characterized via X-ray photoelectron spectroscopy (XPS). The surface atomic composition of the samples calculated from XPS data is given in Table 1. The data show that Al, Si, and O are the main atoms on the surface of coated samples while the content of Ti is significantly decreased in these samples. The surface composition of A1 mainly consists

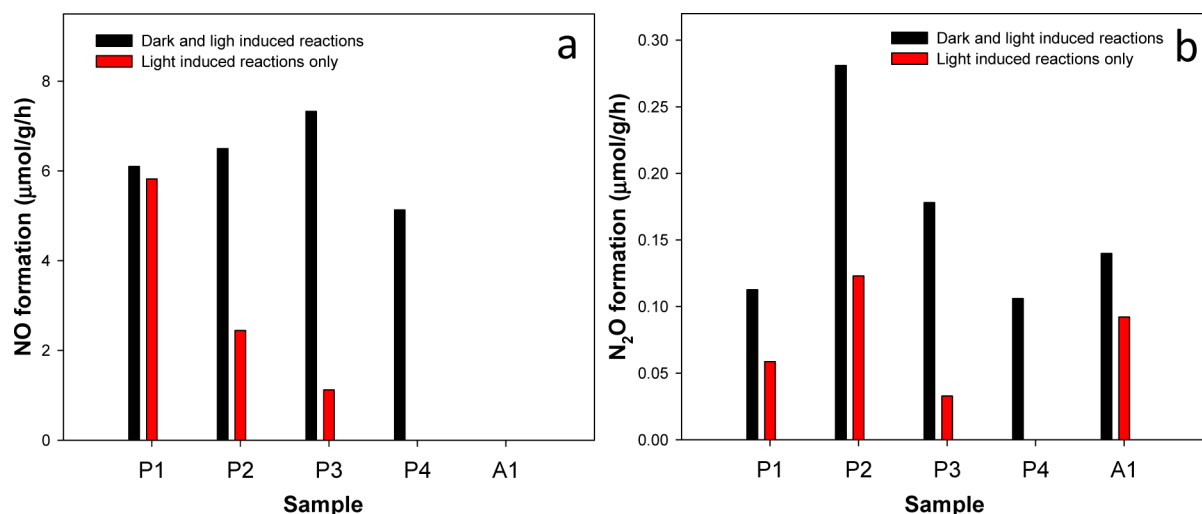


Figure 4. Formation rates of NO (a) and N₂O (b) of the conversion of NO₂ over different catalysts under UV illumination. The black bars are the overall formation rates of the gases. The red bars are the net formation rates contributed by light-induced reactions. These rates are calculated by subtracting the formation rates in dark conditions from the overall rate under UV illumination.

of Ti and O whereas the surface of P1 contains also Al on the surface. For the coated samples, P2 and P4 both show the Al:Si atomic ratio close to 1:1 while more Al appears on the surface of P3 compared to Si (Al:Si \sim 3.5:1). Because XPS analyzes principally the atoms near the surface of the particle due to the limited penetration of the electron beam (\sim 5 nm), the predominant content of Al and Si compared to Ti demonstrates well-coated layers of alumina and silica on the surface of TiO₂. Among the coated samples, P4 shows the highest (Al + Si):Ti ratio (17.5:1), indicating its thicker shell compared to those of P2 and P3 ((Al + Si):Ti ratio of 9:1).

Conversion of NO₂ on Coated and Uncoated TiO₂. It has previously been documented that the interactions of NO₂ with metal oxide surfaces in atmospheric conditions generally produce nitrate ions adsorbed on solid surfaces as the main products.^{11,27} On the other hand, the gas-phase products of this process are varied and strongly dependent on the reaction conditions. The present study focused on analyzing the gas phase products of the interaction of NO₂ with uncoated and alumina- and silica-coated TiO₂ in the dark conditions and in the presence of UV illumination. The reactions were carried out in the presence of oxygen and in the absence of moisture. From the analysis based on FTIR coupled with a long path length gas detector, we observed the formation of NO and N₂O as two main products under the reaction conditions.

Figure 3 shows the formation rate of NO when NO₂ gas with concentration of 10 ppm in air is passed through the reactor containing 5 g of catalyst without light illumination. It can be observed that the surfaces coated with alumina and silica clearly affect the formation rate of NO. The NO formation rate on uncoated TiO₂ P1 sample is relatively small (0.28 μmol/g/h). The A1 sample shows no NO formation in the dark. In contrast, the coated samples exhibit higher NO formation rates of 4.05–6.21 μmol/g/h, more than an order of magnitude higher than that of uncoated TiO₂ P1.

N₂O formation when NO₂ interacts with the catalysts under dark conditions is depicted in Figure 3b. Compared to the NO formation rate, the formation rate of N₂O is much lower. In addition, N₂O formation rates on coated and uncoated samples are comparable to those in the case of NO formation. As can be seen from Figure 3b, the uncoated samples P1 and A1 exhibit

rates of 0.054 and 0.048 μmol/g/h, respectively. For the coated samples, the N₂O formation rates are in the range of 0.106 and 0.158 μmol/g/h, which are 2–3 times higher than those of uncoated samples.

Figure 4 displays the formation rates of NO and N₂O when NO₂ gas reacts with the material in the presence of UV illumination. It can be seen that UV illumination strongly affects the formation of NO on both coated and uncoated TiO₂ materials (Figure 4a). P1 shows a significant increase in NO formation rate as compared to the reaction in the dark. The contribution of the light-induced reactions to the NO formation rate is calculated to be 5.82 μmol/g/h. This rate is more than 20 times higher than the NO formation rate originating from the dark reactions (0.28 μmol/g/h). In contrast, no NO formation was observed on the anatase A1 sample under UV illumination. For the coated samples, the effect of light-induced reactions is also different. While the UV illumination shows no improvement in the NO formation rate over the P4 sample, the overall NO formation rate on the P2 sample is greatly enhanced in the presence of UV light.

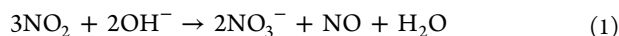
The N₂O formation rate over different catalysts studied is shown in Figure 4b. The data points out that the UV illumination greatly affects the formation of N₂O over uncoated samples. As seen in Figure 4b, the contribution of light-induced reactions to the formation of N₂O is higher than that of the dark reaction over uncoated samples. In the case of coated samples, the presence of UV light enhances N₂O formation rates on P2 and P3 samples, while no enhancement is observed in the case of the P4 sample.

4. DISCUSSION

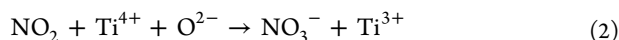
The formation of gas-phase products in the reaction between NO₂ and solid surface is strongly influenced by reaction conditions, especially the presence of molecular oxygen and water. Underwood et al. studied the reaction of pure NO₂ gas on Al₂O₃, Fe₂O₃, and TiO₂ and found NO to be the main product in the gas phase along with a small amount of N₂O.¹⁰ No HONO or HNO₃ was detected in the gas phase. However, when NO₂ is in contact with Al₂O₃ saturated with water vapor, NO and N₂O were not observed in the gas-phase products. On TiO₂, gas-phase products including NO, N₂O, and HONO

have been observed when NO₂ interacts with its surface in different conditions.¹¹ In the present study, we found NO as the main product in the gas phase along with N₂O as minor product when the reaction was conducted under dry conditions and in the presence of oxygen.

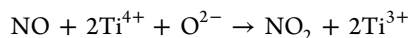
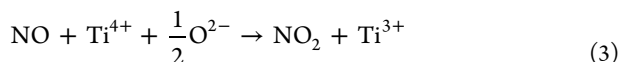
Reaction Mechanism for NO Formation. Without the UV light illumination, the conversion of NO₂ originates mainly from the reaction of NO₂ with the solid surface. Thus, the surface area of the catalysts greatly affects the reaction rate. Given that the surface area of the coated samples is just 2 times higher than that of uncoated sample (P1) (Table 1), the much higher NO formation rates of coated samples compared to uncoated ones cannot be explained based on surface area alone. In addition, although A1 exhibits a very high surface area, no NO formation was observed on this sample. It is well established that on the surface of amorphous metal oxides the NO₂ mainly reacts with surface hydroxyl group to produce NO₃⁻ and NO by following reaction:



On the surface of crystalline metal oxides such as Al₂O₃, Fe₂O₃, Cr₂O₃, and TiO₂, NO₂ can also interact with lattice metal and oxygen ions to form adsorbed nitrate. In the case of crystalline TiO₂ surface, the following reaction is expected:^{28–30}



Gas-phase NO can also interact with lattice Ti⁴⁺ and O²⁻ to produce Ti³⁺ and NO₂ by eq 3:³⁰



The generated Ti³⁺ can be oxidized by oxygen to produce an oxygen anion which can rapidly oxidize nitrogen oxides to form nitrate:^{14,22}



Reactions 1–5 provide a means of explaining the influence of a coating layer on the NO formation rate in the dark. As evidenced from XPS and HRTEM, the coated samples consist mainly of amorphous silica and alumina on the surface. Thus, the reaction of NO₂ on alumina–silica mixture mainly follows reaction 1, which leads to the formation of nitrate and NO. The uncoated samples with a crystalline TiO₂ surface are expected to facilitate reaction 2, producing nitrate on the surface of TiO₂. Furthermore, once produced, NO can also be consumed following reactions 3 and 5. This mechanism explains the low NO formation rate on the surface of crystalline TiO₂. It was suggested that the conversion of NO₂ depends on the surface acidity of the metal oxide surface.³¹ In our study, all the samples exhibit different surface chemical compositions which may lead to the differences in their surface acidity in which TiO₂ exhibits much higher acid strength than alumina and silica.^{32,33} Thus, we propose that a mixture of alumina–silica with lower acidity may favor the adsorption of acid gas NO₂ on their surfaces and enhance NO₂ conversion.

In addition to the reactions under dark conditions, the conversion of NO₂ on the surface of TiO₂ can also be initiated by the generation of electrons (e⁻) in the conduction band and

the holes (h⁺) in the valence band of TiO₂ upon bandgap illumination with UV light. Under these conditions, the e⁻ and h⁺ can react with adsorbed species to induce several reactions. When NO₂ is in contact with TiO₂ surface in the presence of UV illumination, the following reactions can occur:^{17,20}



In the presence of oxygen, the generated e⁻ is rapidly quenched by O₂ following the equation:



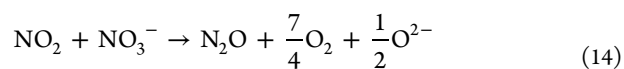
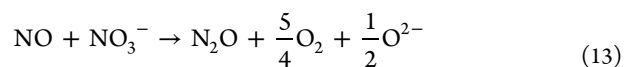
Hashimoto et al.¹⁴ used electron spin resonance spectroscopy to monitor the reaction of NO and O₂⁻ and suggested that O₂⁻ reacts easily with NO to form NO₂ and NO₃⁻ at room temperature. Ibusuki et al. investigated the photocatalytic oxidation of NO on anatase TiO₂ and also found a rapid conversion of NO to NO₃⁻ in the presence of molecular oxygen. In our experiments, the NO₂ conversion was conducted in the presence of oxygen. Thus, the generated electrons on the surface of TiO₂ rapidly reduce the oxygen adsorbed on TiO₂ surface to produce oxygen anion according to eq 12. The NO gas, if produced and adsorbed on TiO₂ surface, may be reoxidized to nitrate according to reaction 5. This mechanism explains well the absence of NO product on A1 under UV illumination and in the presence of excess oxygen.

In contrast to A1, the P1 sample, which includes alumina on the TiO₂ surface, exhibits a significant increase in the NO formation rate under UV illumination. We propose that the presence of alumina on the surface of rutile TiO₂ helps to attract more NO₂ to the surface of the catalyst but does not block the reaction of generated electron from TiO₂ with the adsorbed gas (NO₂) (reaction 8). Previous studies have pointed out a significant increase in the formation rate of nitrate and NO on the surface of alumina when NO₂⁻ is formed on the oxide surface. This was explained via reaction 10.⁹ In this case, the generation of NO₂⁻ from photoelectrons substantially influences the formation of NO since NO can be produced from NO₂⁻ by either reaction 10 or 11. This mechanism can also explain the effect of UV illumination on coated samples. In the P4 sample, the large amount of alumina–silica (i.e., the thicker shell) on the surface (as indicated from XPS results) may increase NO₂ on the surface. This shell could be so thick as to prevent completely the interaction of generated charges and adsorbed species. Thus, no obvious increase in the reaction rate could be observed under illumination. On the other hand, P3 and P2 with its smaller amount of alumina–silica coated on the surface may still enable the interaction electron and hole with NO₂ and, hence, can increase NO formation. These results are of interest since they suggest avenues by which to tune the reactivity of TiO₂ in NO₂ conversion by controlling its surface coverage with metal oxides.

In addition to reactions induced by photogenerated electrons and holes, several nitrogen species can also undergo the

photolysis process in the presence of UV light illumination. It has been observed that nitrate adsorbed on alumina surface can undergo a photolysis process to produce NO, NO₂, and N₂O as gas-phase products under UV illumination.²⁶ Bedjanian et al. studied the interaction of NO₂ with TiO₂ surface under UV illumination and suggested that the heterogeneous photolysis of nitrate is too slow compared to the conversion of NO₂ to produce gas-phase products. Moreover, in the presence of oxygen, the main product in the gas phase is NO₂, and much less NO and N₂O were produced.¹⁷ Thus, we can conclude that the effect of photolysis of nitrate on NO formation is negligible in our experimental conditions.

Reaction Mechanism for N₂O Formation. N₂O is well-known as an important greenhouse gas and is involved in the loss of stratospheric ozone.¹ The formation of N₂O by the heterogeneous reaction of NO₂ and TiO₂ is thus of interest. Previous studies on the interaction of NO with TiO₂ surface suggested that N₂O can be formed when NO is adsorbed on the surface of TiO₂.¹⁰ However, this reaction cannot explain the formation of N₂O on A1 sample in our experiment because NO is not produced on A1. It has been also found that the formation of N₂O when NO₂ is in contact with TiO₂ surface under illumination was independent of the concentration of NO formed.¹⁷ Malecki and Malecka investigated thermal decomposition of nitrate and found the formation of N₂O. These authors proposed that N₂O can be produced by the reaction of NO and NO₂ with nitrate as follows:³⁴



On the basis of our experimental results, we argue that the formation of N₂O through reactions 13 and 14 is plausible on coated samples as both NO and NO₂ are present in the gas mixture during the reaction. However, reaction 13 is not likely to occur on uncoated samples as a small amount of NO was produced in the dark condition.

Under UV illumination, most of the samples exhibit increased N₂O formation compared to their rates in the dark. Among them, the A1 sample shows the highest increase. It can be concluded from the reactions 13 and 14 that the formation rate of N₂O depends on the amount of nitrate adsorbed on solid surface. As discussed earlier, the A1 can easily oxidize NO and NO₂ to nitrate under illumination and in the presence of O₂. Thus, it is expected that a larger amount of nitrate will be produced on the surface of A1 in the presence of UV light compared to that in the dark condition. This mechanism can explain the significant increase in N₂O formation under UV illumination.

Atmospheric Implications. Titanium dioxide is a key component in white paint. Each liter of high quality exterior paint contains ~360 g of TiO₂ and can cover an area of ~10 m². Hence, with an annual consumption of an estimated 30 billion liters of paint, we wished to estimate whether the reactivity of TiO₂ toward atmospheric gases could potentially lead to a quantitatively appreciable on the environment.

From the data obtained, we can roughly extrapolate the formation of NO and N₂O in the dark and under the illumination using UV light (wavelength <413 nm) from sunlight based on a real average NO₂ concentration of 18 ppb. The estimation was based on two assumptions: (i) the

quantum yields of UV light with different wavelength in the reaction of NO₂ on TiO₂ are similar, and (ii) the reaction of NO₂ on TiO₂ is first-order. The results are documented in Table 2. Although these estimates are necessarily rough, the

Table 2. Estimation of the NO and N₂O Formation Rates in Atmospheric Conditions

sample	NO formation		N ₂ O formation	
	g/kg/year ^a	mg/m ² /year ^b	g/kg/year ^a	mg/m ² /year ^b
P1	0.636	22.92	0.039	1.43
P2	1.860	67.04	0.110	3.96
P3	2.615	94.14	0.091	3.26
P4	2.103	75.74	0.063	2.27
A1	0.000	0.00	0.040	1.45

^aThe calculation is based on the following assumption: (i) the solar power is 100 mW/cm²; (ii) all TiO₂-photoactive UV light in sunlight (wavelength <413 nm) exhibits similar quantum yield; (iii) the illumination time in a day is 8 h; (iv) the real NO₂ concentration in the air is 18 ppb. ^bThe data are calculated from (a) with an assumption that each square meter is covered by 36 g of TiO₂ (this is based on the fact that 1 L of paint containing 360 g of TiO₂ and can cover 10 m²).

values here still indicate that the formation rates of NO and N₂O are low. The highest NO formation rate was obtained on P3 (94.14 mg/m²/year) while P2 exhibited the highest N₂O formation rate of 3.96 mg/m²/year. These results are also consistent with the previous studies in which the formation rate of reduced gases (NO, N₂O) was small when NO₂ interacts with TiO₂ under sunlight illumination and in the presence of oxygen.^{4,18,20} Given the fact that most NO and N₂O formation originated from dark reactions (reactions 1 and 14), the formation of nitrate on coated TiO₂ samples, which is linearly proportional to the amount of NO and N₂O produced, is thus in the range of few tens of milligrams per square meter per year. Thus, though the coating of TiO₂ with alumina–silica enhances the formation of NO, NO₂, and NO₃⁻ in the dark, it can significantly reduce the formation of nitrate under illumination.

5. CONCLUSIONS

The formation of gas-phase products when NO₂ interacts with the surface of TiO₂ coated with a mixture of alumina and silica in the presence of oxygen was investigated. The results show a strong influence of surface modification on the reactivity of TiO₂ toward NO₂. Specifically, coating TiO₂ with alumina–silica mixture greatly enhances the formation of NO and N₂O in the dark condition. Under UV illumination, the effect of coating layer depends upon its thickness and composition. We have found that a small amount of alumina on the surface of rutile TiO₂ significantly improves the formation of NO under illumination while thick coated layer on the surface of TiO₂ completely suppresses its light-induced reaction. The results reported here demonstrate that the nitrogen oxides produced in the gas phase on the surface of TiO₂ could be tuned by modifying the surface of TiO₂ with metal oxide such as alumina and silica. Overall, rates of conversion (on the order of mg/m² paint/year) indicate that these materials are not expected to have a quantitatively significant impact on NO_x levels in the environment.

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Notes

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