

Atmos. Chem. Phys. Discuss., referee comment RC1  
<https://doi.org/10.5194/acp-2022-6-RC1>, 2022  
© Author(s) 2022. This work is distributed under  
the Creative Commons Attribution 4.0 License.

## Comment on acp-2022-6

Anonymous Referee #1

---

Referee comment on "The positive effect of formaldehyde on the photocatalytic renoxification of nitrate on TiO<sub>2</sub> particles" by Yuhan Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-6-RC1>, 2022

---

This manuscript investigated the effect of HCHO on the photocatalytic renoxification of nitrate on TiO<sub>2</sub> particles. The investigated system is interesting. However, the experimental design has so many defects. More experiments and verification are needed to support the conclusion.

Major comments:

- Methods: Line 103: 400 L chamber is usually not enough for the investigation of heterogeneous reactions. Besides, only 250 L air was injected into it, which would increase the wall effect of chamber. Line 105-106: How did the author control the chamber temperature? It is well known that the chamber temperature will increase when turn on the lights. Line 111-112: the light intensities for the tube and LED lamp were different, so how to compare their results? Why was only the results in 3.1 obtained under the irradiation of tube lamps? What was the meaning for introducing two kinds of lamps in the smog chamber?
- Important defect of this article is the composition of the mixture in the part of "2.2 nitrate-TiO<sub>2</sub> composite samples": "TiO<sub>2</sub> was simply mixed in nitrate solutions at the desired mass mixing ratio to obtain a mash. The mash was dried at 90 °C and then ground carefully to ensure a uniform composite of particles." How did the author ensure that the particles are uniform composite of nitrate and TiO<sub>2</sub>? Did the author do some experiments to confirm these? For example, in the reference of Ma et al (EST, 8604-8612, 2021), the nitrate and TiO<sub>2</sub> mixture was **dripped onto a quartz tube inner all**, then images and Raman spectra of single composition and mixture were analyzed, and mixture were confirmed to form. However, in this work, the generation method of mixture particles is different from that of Ma's work, and these mixture particles are **sprayed by synthetic air into PVF bag**. No experiments have been given to confirm the composition of the mixture particles in the chamber. In my opinion, this method can't generate a uniform composite of nitrate and TiO<sub>2</sub>!!! The composition and the nitrate content are the most important quantitative method factors of all the experiments in the article. If the composition and nitrate content can't be control, how to compare the NO<sub>x</sub> concentration in different experiments? Then, all the results are not convincing!!!

- Another important defect of this article is the quantitative method of NO<sub>x</sub> concentration. As shown in Ma's work, they used the normalized concentration (ppb/mg) to quantify NO<sub>x</sub>. However, this work just used the NO<sub>x</sub> concentration (ppb) to compare different experiments, which meant that if more reactants were added in the chamber, the generated NO<sub>x</sub> concentration would be higher. The initial mass concentration of particles was 300 mg/m<sup>3</sup> (75mg/250L), and the concentration of HCHO was 10 ppm, which were much higher than that in the real environment and resulted in that the obtained results could not be directly used for an analogy to real environment. The results with ppb as unit are meaningless to reflect their influence in the real atmosphere. Were the particles kept the same in different experiments during the reaction? The author mentioned that the wall loss of particle in the smog chamber was very high at the beginning. And the wall loss for different kinds of particles and for the same kind of particles in different experiment (maybe affected by the conditions of the smog chamber wall) should be different. How did the author ensure that the particle distributions were the same in different experiments when turned on the light? Besides, the surface area, as an important factor in heterogeneous reactions, has not been detected in the experiments. Different surface areas directly affect the irradiation surface of TiO<sub>2</sub>, the uptake of HCHO and the release of NO<sub>x</sub>. The missing information of surface area would result in the large uncertainties in the experiments. At least, the authors should give a normalized NO<sub>x</sub> concentration, then different experiments can compare with each other and give the reasonable results and reflect the influence in the real environment.
- Gas HCHO and mixture particles of TiO<sub>2</sub> and nitrate were contained in the system. Although some controlled experiments were conducted, the role of TiO<sub>2</sub> and HCHO still could not be isolated. A series of important experiments such as HCHO and single nitrate particles under irradiations are needed.
- All the proposed mechanisms couldn't be well supported only by the changes of NO<sub>x</sub> concentration. This work and Ma's work indicate HONO, HNO<sub>3</sub>, NO<sub>3</sub> radical, NO<sub>x</sub> could form in these reaction systems. However, HONO, HNO<sub>3</sub>, NO<sub>3</sub> radical could lead the overestimation of NO<sub>2</sub> concentrations by chemiluminescence method. How did the authors exclude the effect of these species? Besides, most important products such as NO<sub>3</sub>, HNO<sub>3</sub>, HONO were not detected in the experiments except OH radical. How did the authors make sure that the reaction pathway followed the proposed mechanisms? It is well known that TiO<sub>2</sub> can photocatalysis HCHO, can this reaction affect the formation of NO<sub>x</sub>?
- The mixture of HNO<sub>3</sub> and TiO<sub>2</sub> was used to support that HNO<sub>3</sub> was an important intermediate to form NO<sub>x</sub>. However, this logic is not right. If it is right, then any N-contained components mixed with TiO<sub>2</sub> that enhanced the generation of NO<sub>x</sub> could be thought as the intermediates of NO<sub>x</sub> formation. The direct way to identify the intermediates is to measure them such as FTIR/DRIFTS to measure the adsorption products.

#### Minor comments:

- Abstract: many sentences are confusing me! I can't understand what the main meaning of the work. What's the main results. The languages need to be improved.
- "photocatalysis", "photolysis", "photocatalytic", "photochemical" appeared in the manuscript everywhere, the author should make sure the exact meaning of these words and give the right usage of these words.
- Line 232-233, the photodegradation of HCHO on TiO<sub>2</sub> is not zero-order reaction kinetics, the curve is not a line as shown in Figure S6, which decreased slowly and then

fast. The reason for it should be the large amount of adsorption of HCHO on the particle during the long-time injection of HCHO. Besides, the continuous wall loss of particle would result in the change of kinetic coefficient. The concentration of particles and HCHO were too high, and the injection time was too long to give clear kinetic parameters. Generally, the photocatalytic process is supposed to be a first order reaction.

- I can't understand why the authors used  $\text{KNO}_3$  and  $\text{HNO}_3$  to mixture with  $\text{TiO}_2$ . In Ma's work, they indicated the  $\text{NO}_x$  concentration formed from  $\text{KNO}_3$  was the lowest.  $\text{KNO}_3$  only accounts for small proportion in the atmospheric particles.  $\text{HNO}_3$  is acid species and can react with  $\text{TiO}_2$ , which would result in the component changes in this mixture particles. I think that the components in this mixture particles were different from the discussion in the article.
- OH radical was measured by ESR in this study. However, the role of OH radical has not been discussed. And the OH radical generated in different particles and under different conditions have not been compared and analyzed. Besides,  $\text{NO}_3$  radical was proposed to be the important intermediates in the reaction. Why did not the authors measure  $\text{NO}_3$  radical?
- Weight percentage was used to quantify nitrate in the mixed particle. However, different nitrate has different molecule weight, which would result in that the molar concentrations of different nitrates with the same weight percentage were different. For example, the molar concentration of N in 4 wt %  $\text{HNO}_3$ - $\text{TiO}_2$  is higher than that of N in 4 wt %  $\text{KNO}_3$ - $\text{TiO}_2$ . This effect should be considered in the formation of  $\text{NO}_x$ .