Response to the reviewer's comments:

Referee #2: General Evaluation

Liu et al. investigated the possible renoxification processes occurring on TiO_2 *particles and mineral dust particles in presence of adsorbed nitrate, or* HNO_3*, in presence of HCHO. They suggest that HCHO and* TiO_2 *have a significant synergistic effect on the photocatalytic renoxification via a* NO_3*-*NO_3*-HCHO-*HNO_3*-NOx pathway, in which adsorbed HCHO may react with nitrate radicals through hydrogen abstraction to form* HNO_3 *on the surface, resulting an enhanced generation of NOx.*

Overall this is an important topic, which certainly falls within the scope of journal Atmospheric Physics and Chemistry.

Response:

Thanks for your comments, which will be all valuable and very helpful for revising and improving the manuscript, as well as the important guiding significance to our researches. We have thought deeply about the experimental design, and answer the comments point by point.

Comments on Preprint acp-2022-6:

1. The experiments presented here were performed in a simulation chamber consisting of a 400 L polyvinyl fluoride (PVF) bag filled with synthetic air. In such a small baga, the life time of particles is expected to be very short, as shown also in figure S2. Surprisingly, the authors do observe, after some induction time, a stable size distribution over hours. How can this happen? Is it an indication of some dynamic interactions with the chamber's walls, during which particle adsorb and desorb constantly? Such process may be induced to some air turbulences around the bag, or through its deflation during the experiments (by the way, was the bag closed and its volume shrinking or was it flushed by pure air all the time during the experiments?). Anyhow, this is a strong indication that wall effects may play a significant role in the reported experiments. Therefore, a thorough discussion of these effects has to be included in the manuscript.

Response:

Thanks for your comments. We are sorry that the description of operating procedures is not so clear. So we modified this in the revised manuscript. Here, we would like to describe the operation briefly. The sequence of the experimental operation of the chamber is as follows: cleaned by deionized water, dried totally, then inflated by synthetic air to a certain volume, then HCHO introduction, and then particles introduction instantly by a high pressure air flow. After the concentrations of both HCHO and particles became stable, the lamps were turned on and the concentrations of NO_x were monitored. The chamber was closed during the entire experiment. Once the particles entered into the chamber, the number concentration began to decrease due to the wall effect. After 30 min, the size distribution of both KNO_3-TiO_2 and TiO_2 particles got stable and can sustained for several hours (with Figures 1-3 shown below). The left picture in the following Figure 2 shows the first 60 min of the size distribution in the dark, and the right picture of the size distribution during the irradiation. Figure 3 is another batch experiment of TiO_2 in the chamber with the same operation, and it shows very similar size distribution from 0-60 mins and 120-180 mins. During the experiment, we strictly controlled the same experimental condition before the start of each experiment and turned on the lamps only after the particles and HCHO concentration reached stability.

The corresponding revisions are as follows: (1) The injection of the particles has been emphasized in section 2.3 of the revised manuscript: "Particles were instantly sprayed into the chamber by a transient high-pressure airflow"; (2) The sentences "For the chamber operation, we completely evacuated the chamber after every experiment, then cleaned the chamber walls with deionized water and then dried by flushing the chamber with ultra-zero air to remove any particles or gases collected on the chamber walls" was added to the section 2.3 of the revised manuscript.

In addition, we checked our size distribution data of different samples, and found that the number concentration is not that high and usually around 4000 particle/cm^{-3} when reaching stability. So Figure S2 in the original manuscript was deleted and replaced by the following Figure 1 (Figure S3 in the revised supplement).

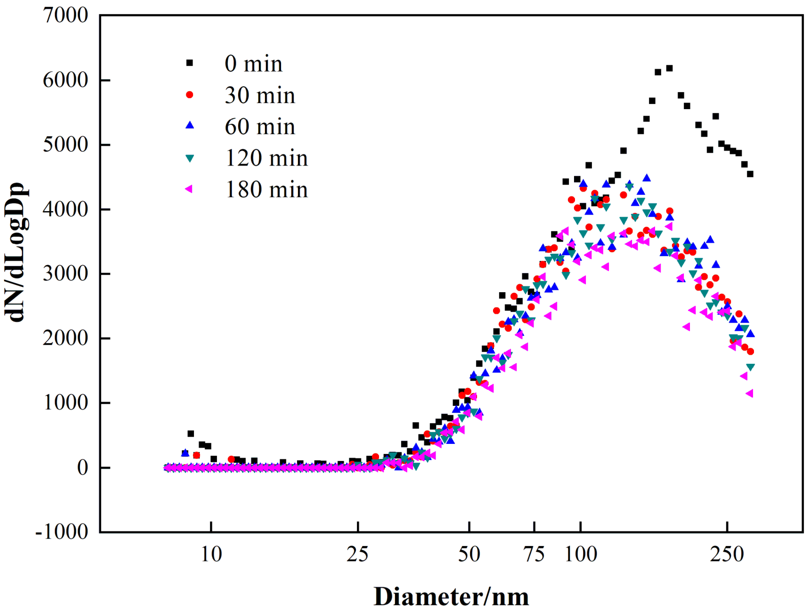

Figure 1. Changes of particle size distribution of 4 wt.% KNO_3-TiO_2 particles in environmental chamber with time.

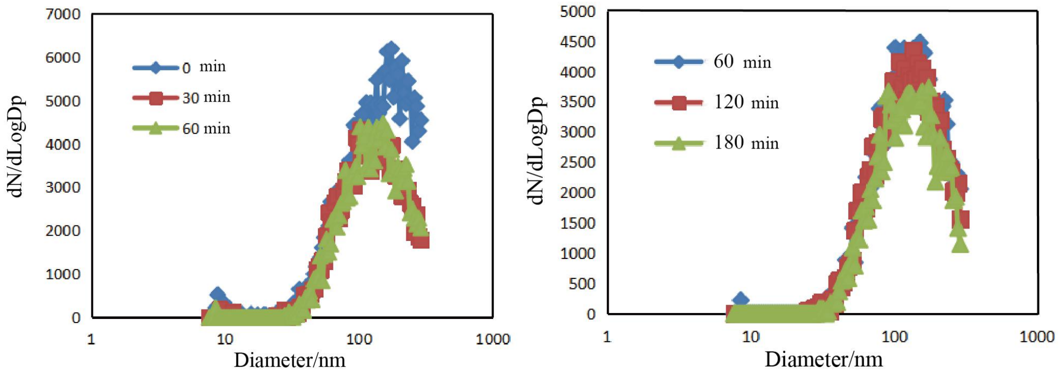

Figure 2. Changes of particle size distribution of TiO_2 particles in environmental chamber with time. Left: Before irradiation; Right: After irradiation.

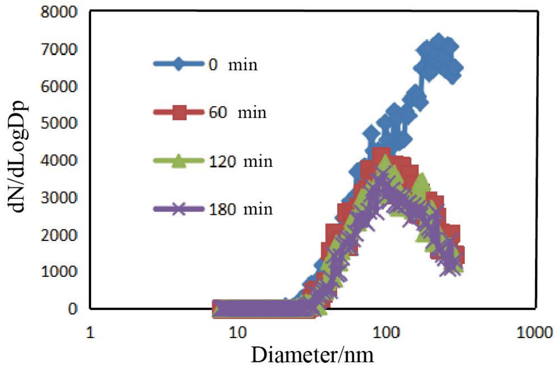

Figure 3. Changes of particle size distribution of TiO_2 particles in environmental chamber with time (Another batch experiment).

2. The main conclusion of this work is that adsorbed HCHO reacts with adsorbed nitrate radicals, promoting NOx formation. This assumes that this reaction is faster than the one of HCHO with the photochemically generated holes on the surface of the mineral. Is this justified by any means? HCHO being efficiently degraded on illuminated TiO_2, one would expect that this VOCs may compete with the nitrate anions to react with the holes, with the synergy between nitrate anions and HCHO vanishing at low surface coverage (where both compounds would react with the holes with no interactions with co-adsorbed species). Is this observed here?

Response:

Thanks for your comments. As the reviewer mentioned, HCHO can react with the photochemically generated holes on the surface of the mineral. The photodegradations of HCHO on TiO_2 and KNO_3-TiO_2 particles were observed in this study. As shown in text line 230-239 of the original manuscript: "*Atmospheric trace gases can undergo photocatalytic reactions on the surface of TiO_2 (Chen et al., 2012). As the illumination time increased, the concentration of HCHO showed a linear downward trend, which was consistent with zero-order reaction kinetics (Figure S6). The zero-order reaction rate constants of HCHO on TiO_2 and 4 wt.% KNO_3-TiO_2 particles were 9.1×10^{-3} and 1.4×10^{-2} ppm min^{-1}, respectively, which were much higher than that for gaseous HCHO photolysis (Shang et al., 2017). We suggested that the produced $NO_3\cdot$ contributed to the enhanced uptake of HCHO. Therefore, we suggest that $NO_3\cdot$ production contributed to enhanced HCHO uptake. Future studies should explore whether HCHO affects the photocatalytic renoxification of NO_3^--TiO_2*". Besides the photodegradation of HCHO on excited TiO_2 particles, higher photodegradation rate of HCHO was observed on KNO_3-TiO_2 particles. As for if there is a simultaneously decrease of nitrate, we once compared the absorption spectra of the extracts of KNO_3-TiO_2 particles before and after reactions, with results shown below as Figure 4. It can be seen that nitrate content was decreased after reaction, meaning the vanishing of the nitrate.

By now, we do not know which of the reactions is faster ("HCHO+hole" or "HCHO+NO_3 radical"), but due to the high amount of both HCHO and TiO_2 used in this study, on one side, there are enough holes to react with HCHO and nitrate at the same time, and on the other side enough remaining HCHO to react with NO_3 radical.

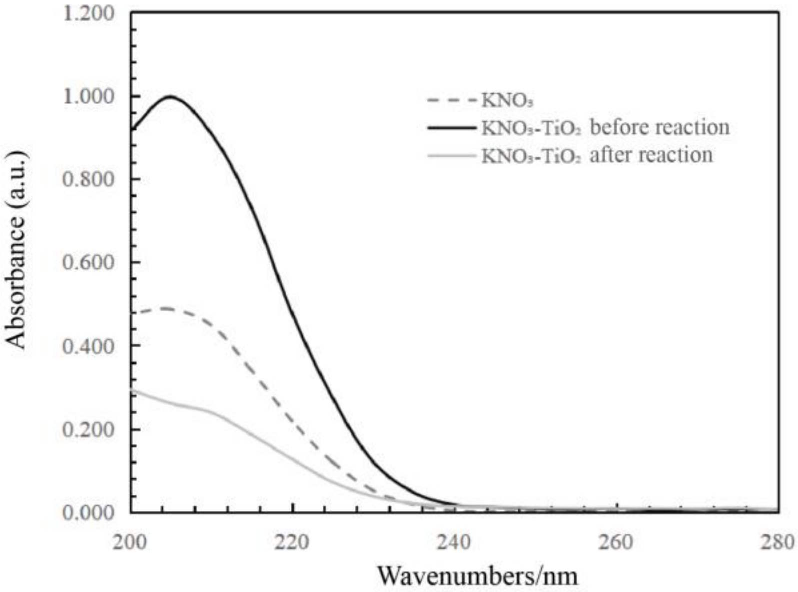

Figure 4. Absorption spectra of the extracts of KNO_3-TiO_2 particles before and after reactions.

3. Spraying mixture of SiO_2 and TiO_2, would result in an externally mixed aerosol, isn't it? Then it should represent an experiment with the TiO_2 particles simply being diluted as compared to the pure TiO_2 experiment.

Response:

Thanks for your comments. There are two reaction systems in our experiments. The first system, in which HCHO was not introduced, was intended to investigate the positive effect of TiO_2 on the renoxification process. In this system, we used 4 wt.% KNO_3-SiO_2 and 4 wt.% KNO_3-TiO_2 (1 wt.%)/SiO_2. Here TiO_2 (1 wt.%)/SiO_2 was prepared first and then 4 wt.% KNO_3 was composited. In the second system, HCHO was introduced to investigate the synergistic positive effect of TiO_2 and HCHO on the renoxification process. The samples used in this system were 4 wt.% nitrate-TiO_2. Here 4 wt.% nitrate was composited to the pure TiO_2 particles. Note that, in the first system, the main particle is SiO_2 and the content of TiO_2 is only 1 wt.% relative to SiO_2. While in the second system, the main particle is TiO_2. So there is a large difference in the TiO_2 mass in these two particles. It is not a simple dilution of TiO_2 with SiO_2.

4. An effect of acidity is observed and explained by the enhanced photolysis of HNO_3*. Could an alternative explanation arise for the chemistry of* O_2^-*? This superoxide would react with* H^+ *inducing* HO_2 *chemistry that may change a series of surface reactions. Could the authors comment on that?*

Response:

Thanks for your comments. Our experiments were performed under dry conditions, so there is little H^+ to react with O_2^- to produce HO_2^-, and the mass release of NO_2 was ascribed to the photolysis of HNO_3. However, in our study of relative humidity as an influencing factor, there are some possible effects arising from O_2^-. Under high humidity, adsorbed H_2O can behave as scavenger of photogenerated holes (h^+), so as to make photogenerated electron (e^-) reacted with oxygen, resulting in the generation of $O_2^-\cdot$ (Eq. 1). $O_2^-\cdot$ can combine with H^+ to generate $HO_2\cdot$ (Eq. 2). Subsequently, NO undergoes a two-step photocatalytic degradation on TiO_2: oxidation of NO by $HO_2\cdot$ to NO_2 (Eq. 3) and oxidation of NO_2 by $OH\cdot$ to HNO_3 (Eq. 4) (Dalton et al., EP, 2002, 120: 415-422; Devahasdin et al., J Photoch. Photobio. A, 2003, 156: 161-170). Therefore, higher relative humidity can affect NO and NO_2 production due to HO_2 chemistry, which has been discussed in section 3.3.3 of the original manuscript.

$$O_2 + e^- \rightarrow O_2^- \cdot \qquad (1)$$

$$O_2^- \cdot + H^+ \rightarrow HO_2 \cdot \qquad (2)$$

$$NO + HO_2 \cdot \rightarrow NO_2 + OH \cdot \qquad (3)$$

$$NO_2 + OH \cdot \rightarrow HNO_3 \qquad (4)$$

Special thanks to you for your good comments.