Response to the reviewer's comments:

Referee #3: General Evaluation

The author reported formaldehyde may have synergistic effect in photocatalytic renoxification of nitrate with TiO_2*, in order to explain the difference between field data and modeling result. The article focuses on the significant synergistic effect, i.e., HCHO and* TiO_2 *have on photocatalytic reactions and providing one possible reaction pathway-* NO_3*-*NO_3*-HCHO-*HNO_3*-NOx. These findings improve the understanding of the role of reactions between organic components and nitrate in the chemical and physical properties of aerosol particles in low relative humidity region. It has significant implication in the research of atmosphere and air pollution, but some issues in the article must be improved. I recommend accept this article after resolve those issues. There are the comments I have for this work:*

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. There are some misdescriptions in the manuscript. Like:

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. (Line 236, Page 12)*

photochemical cycle of HOx radicals in the atmosphere and the formation of (Line 448, Page 25)

Response:

Sorry for our carelessness about these sentences. In the revised manuscript, we have deleted the second half of the first sentence mentioned by the reviewer. The revised sentence is: "*We suggested that the produced* $NO_3\cdot$ *contributed to the enhanced uptake of HCHO*". For the second sentence, HOx means some reactive species such as HO_2 etc. Due to there is not many discussion about HO_2 in the manuscript, we revised the sentence as: "*photochemical cycle of reactive radicals in the atmosphere and the formation of…*"

2. Please explain why 4 wt.% KNO_3-TiO_2(1 wt.%)/SiO_2 underwent reaction to release NOx, while 4 wt.% KNO_3-SiO_2 and 4 wt.% KNO_3-TiO_2 not in same condition.

Response:

Thanks for your comments. In our experiment, two reaction systems existed. The reaction systems and aims of the two kinds of light sources were different, which were summarized in the following Table 1. 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. The light source for this system is tube lamps. In the second system, HCHO was introduced to investigate the synergistic positive effect of TiO_2 and HCHO on the renoxification process. Our samples used in this system study were 4 wt.% nitrate-TiO_2. The light source for this system is LED lamps. LED lamps do not contain visible light component, so the effect of NO_x release from the photolysis of NO_3 radicals under visible light could be excluded. So 4 wt.% KNO_3-TiO_2(1 wt.%)/SiO_2 (or 4wt.% KNO_3-SiO_2) and 4wt.% KNO_3-TiO_2 are not used in the same reaction system. The 4 wt.%KNO_3-SiO_2 did not release NO_x because SiO_2 has no photocatalytic activity, as we discussed in section 3.1 of the manuscript.

Table 1. A comparison of the different particles used.

Light source and Wavelength range	Section	System	Phenomenon	Contents/Implications
TUBE LAMP, 320-400 nm with small amount of 480-600 nm	3.1	4 wt.% KNO_3-SiO_2 (NO HCHO)	No NOx was released	•320-400 nm irradiation cannot make nitrate photolyze, so to exclude the photolysis source of NOx from nitrate. [Fig 1]
		4 wt.% KNO_3-TiO_2 (1 wt.%)/SiO_2 (NO HCHO)	NOx release was observed	•TiO_2 was composited to SiO_2, to see the effect of TiO_2 along with nitrate. •320-400 nm irradiation can excite TiO_2 to generate electron-hole pairs. •Nitrate can react with photogenerated holes to produce NO_3 radicals •480-600 nm irradiation can make NO_3 radical photolyze, generating NOx •Above explanation can be seen in section of 3.1 and the equations 1-4 in the original manuscript.

Section 3.1 proves that NO$_3$ radical can be produced in the condition of “nitrate+ TiO$_2$ (excited by the UV light of the tube lamp)”, then NO$_3$ radical undergo photolysis (under visible light of the tube lamp) to produce NOx. In order to avoid the photolysis of NO$_3$ under visible light, no tube light containing visible light was used any more in section 3.2. The aim of 3.2 is to investigate whether the produced NO$_3$ radical can be captured by HCHO. This explanation can be seen in the first paragraph in section 3.2, that is Line 219-229 of the original manuscript.				
LED LAMP, 350-390 nm	3.2	(WITH HCHO) 4 wt.% nitrate-TiO$_2$	NOx release was observed	350-390 nm irradiation cannot make nitrate photolyze, so to exclude the photolysis source of NOx from nitrate. [Fig S5] 350-390 nm irradiation can excite TiO$_2$ to generate electron-hole pairs, so as to generate NO$_3$ radical. 350-390 nm irradiation cannot make NO$_3$ radical photolyze. NO$_3$ radical can react with HCHO to produce HNO$_{3}$(ads) The observed NOx comes from the photolysis of HNO$_{3}$(ads).
This explanation can be seen in section 3.2, including Fig 2 and equations 5-8.				

3. In Figure S3, the concentration of HCHO and TiO$_2$ particles reached stable in 60 min after introduced into experimental chamber, but other experiments almost stared in -30min, did HCHO and TiO$_2$ have been stable?

Response:

Thanks for your comments. We are sorry to make the reviewer misunderstand the operation sequence of the experiment. Figure S3 in the original manuscript is the conditional experiment results to show the HCHO adsorption in the dark before and after particles injection. We have modified Figure S3, shown below as Figure 1. The operation sequence of the experiment is as follows. HCHO gases was flowed 10 min into the clean chamber firstly under dark conditions. As can be seen in Figure 1, HCHO can get equilibrium around 90 min. After that, no obvious decrease of HCHO was observed meaning that no further HCHO was adsorbed by the chamber. Then the particles were introduced into the chamber instantly. The concentration of HCHO began to decrease upon particles injection and need 60 min to reach its second adsorption equilibrium. After that, HCHO concentration can be maintained in the dark for several hours, indicating no further adsorption of HCHO by the chamber and the particles. In irradiation experiments, we waited for both HCHO and particles to reach stable before turning on the lights. The related description of the operation has been revised in the manuscript. The -30 min in others figures refers to the concentration measurements of NO_2 in the dark, and the adsorption of HCHO or particles was begun long before that.

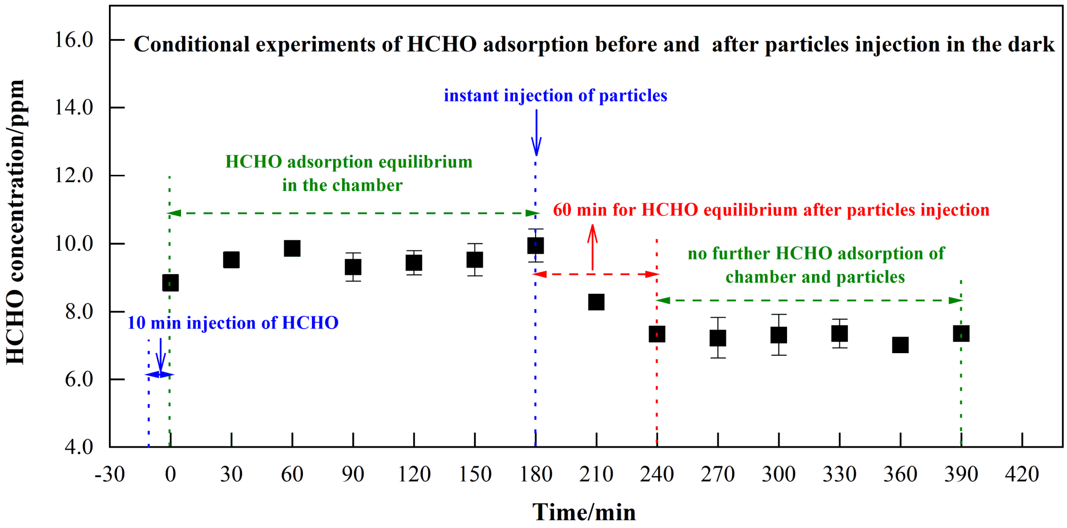

Figure 1. The conditional experiments of HCHO concentration in the environmental chamber in the dark before and after the introduction of particles over time.

4. The BET of TiO_2 nanoparticles is huge, the uptake of HCHO in TiO_2 nano-particles can't be ignored. The photodegradation of HCHO on TiO_2 and 4 wt.% KNO_3-TiO_2 particles should start after adsorption and desorption balance.

Response:

Thanks for your comments. In our study, the uptake of HCHO on TiO_2 nano-particles was considered. As shown in Figure 1 above of conditional experiments of HCHO adsorption in the dark, it needs 60 min (from 180-240 min in the Figure) for HCHO to get stable after the particles' injection. For each experiments, we waited at least 60 min to ensure that the adsorption equilibrium has been reached.

5. In section 3.3.1, 4 wt.% KNO_3-TiO_2 particles release less NOx than Equal amounts of 4 wt.% NH_4NO_3-TiO_2 particles at 293K and 0.8% relative humidity, which may be the result of the Relative molecular mass difference between KNO_3 and NH_4NO_3.

Response:

Thanks for your comments. We agree with the reviewers that different nitrates with the same weight percentage owns the difference in mole of N, which will cause the difference in NO_2 formation. To exclude this effect, we replotted Figure 3 of the original manuscript (here Figure 2 shown below) with mole normalized ppb as the NO_2 formation unit rather than ppb. As can be seen from Figure 2, the main conclusion is the same, with NH_4NO_3-TiO_2 presented higher activity than KNO_3-TiO_2 in the presence of HCHO. The discussion related to this Figure has been modified in the revised manuscript.

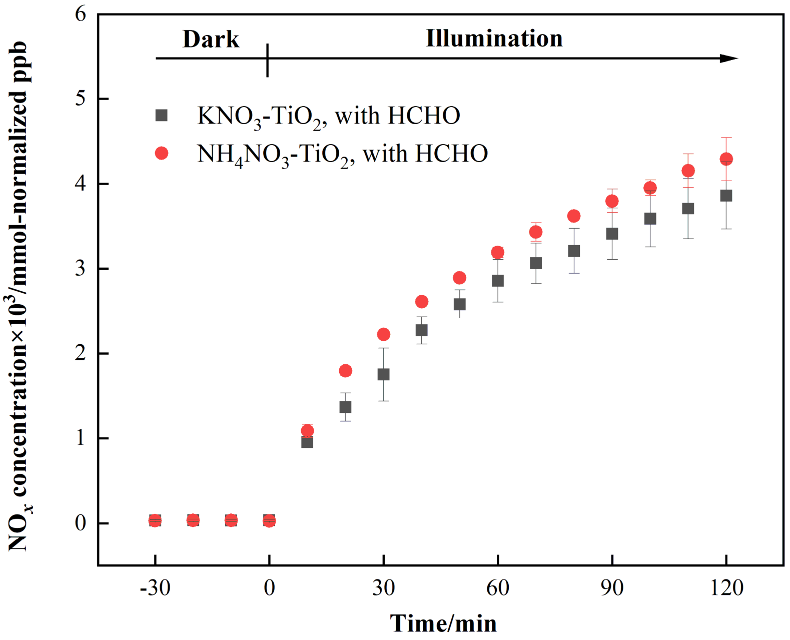

Figure 2. Effect of formaldehyde on the renoxification processes of 4 wt.% NH_4NO_3-TiO_2 and 4 wt.% KNO_3-TiO_2 particles at 293 K and 0.8% of relative humidity. 365 nm LED lamps were used during the irradiation experiment. The initial concentration of HCHO was about 9 ppm.

6. In section 3.3.4. more different initial concentration of HCHO should be test to find out from which content the positive effect become weakening.

Response:

Thanks for your comments. There is an equilibrium of NO_2 release in our reaction system, one is the photocatalytic oxidation reaction between NO_x and ROS (generated from excited TiO_2), and the other is the renoxification of NO_3^--TiO_2 particles. As discussed in the section 3.3.4 in original manuscript, these two competitive reactions will determine the up or down of NO_2.

We measured the variations of HCHO concentration both in its high and low system, with results shown in Figures S6 and Figure 3 below. The rate constant of HCHO decay are 1.4×10^{-2} ppm min^{-1} and 1.3×10^{-3} ppm min^{-1}, respectively. The NO_2 generation rate in Figure S2 and Figure S10 are 1.2 ppm min^{-1} and 0.1 ppm min^{-1}. So the HCHO concentration, HCHO decay rate and NO_2 generation rate all decreased a factor of 10. This coincidence gives us a clue that there may be some connections among these parameters. Another clue is that from Figure S10, it can be seen that the concentration of NO_2 begin to decrease at the time of 50 min, and corresponds to about 0.95 ppm of HCHO (as shown in Figure 3). So it is indicated that below 0.95 ppm of HCHO, the reaction between NO_x and ROS is dominant. More experimental evidences regarding the point of HCHO concentration making positive effect weaken need further investigation. Atmospheric HCHO concentrations are generally very low. However, in cities with high traffic density, because combustion produces emissions, HCHO concentrations will be much higher than normal. In the indoor environment, HCHO levels can increase due to smoking, emissions from gas stoves and furniture, and can reach up to around 0.4 ppm (Formaldehyde. In: Wood dust and formaldehyde. Lyon, International Agency for Research on Cancer, 1995, 217-362). So, we assume that the positive effect of HCHO on the renoxification may still exist at some specific situation with its high concentration.

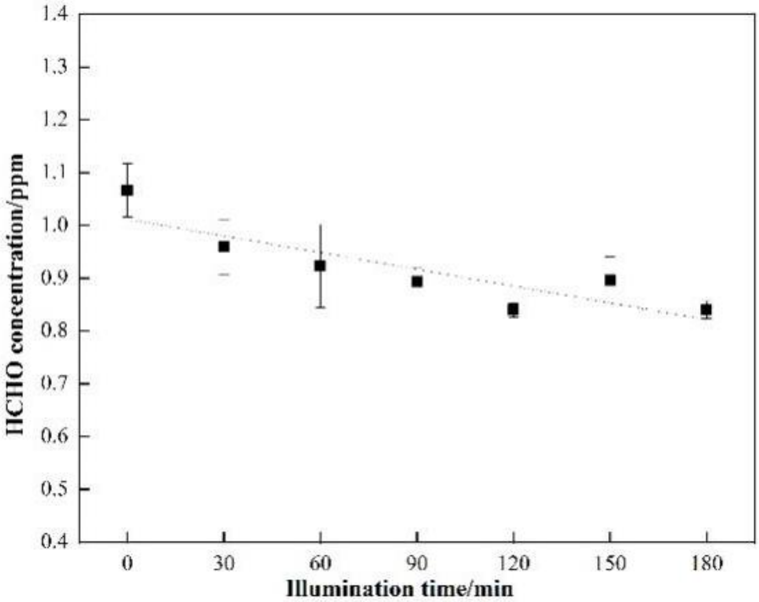

Figure 3. Photodegradation curves of low concentration formaldehyde on 4 wt.% KNO_3-TiO_2 particles under 365 nm LED illumination.

It is worthy of noting that although there usually not so much high concentration of HCHO, there are many other organics in the atmosphere which can provide hydrogen atoms to behave similar role as HCHO. As discussed in line 459-465 of the manuscript: "*The effect of low-concentration HCHO on the renoxification of* NO_3^--TiO_2 *particles requires further investigation. However, many types of organics provide hydrogen atoms in the atmosphere, including alkanes (e.g., methane and n-hexane), aldehydes (e.g., acetaldehyde), alcohols (e.g., methanol and ethanol), and aromatic compounds (e.g., phenol) that react with* $NO_3\cdot$ *to produce nitric acid (Atkinson, 1991). These organics, together with HCHO, play similar positive roles in photocatalytic renoxification and, therefore, influence* NO_x *concentrations*". We also believe that the effect of more different concentrations of HCHO on the renoxification of NO_3^--TiO_2 particles deserves to be studied.

Special thanks to you for your good comments.