August 4, 2022

Editor-in-Chief, Atmospheric Chemistry and Physics

Dear Prof. Ryan Sullivan:

Thank you very much for your kind consideration on our paper “The Positive Effect of Formaldehyde on the Photocatalytic Renoxification of Nitrate on TiO_2 Particles” (Manuscript ID: Preprint acp-2022-6). The comments are very valuable and helpful for revising and improving the manuscript. In the new revised manuscript, we have considered the comments and made revisions accordingly.

We have added the relevant experimental parameters used and stated the limitation and implication of our manuscript in Abstract. Moreover, the pathway has been modified from “NO_3^--$NO_3\cdot$-HCHO-HNO_3-NO_x” to “NO_3^--$NO_3\cdot$-HNO_3-NO_x” together with some explanation for better understanding, and has also been modified in the full text. In the section of Introduction, a specific scenario of low $NO_3^-/(NO_3^-+TiO_2)$ ratio was presented.

Please see the response and the revised manuscript files for details. Thanks a lot for your time and help.

Yours sincerely,

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Comments

The central issue of concern here is how relevant are these experimental particle systems to atmospheric conditions. It is hard to imagine a situation in the atmosphere where you would have mostly just very small TiO_2 particles with lots of HNO_3/nitrate adsorbed, and 100s of ppb of HCHO available to also absorb and participate in the photochemistry.

The abstract should specify the relevant experimental parameters used, especially the high HCHO concentrations used. And also state that these experimental conditions are only proxies or simplified mimics for atmospheric mineral dust that do not necessarily reflect the chemistry that atmospheric mineral dust particles will facilitate. Furthermore, the statement in the abstract "The mass generation of NO_x was suggested to via the NO_3^--$NO_3\cdot$-HCHO-HNO_3-NO_x pathway" is really hard to understand. Please rephrase this to express this statement more clearly.

Please also correct the figure numbering as was noted by the editorial staff: "For the next revision, please renumber the figures in the manuscript. Now you have two figures #5, missing the figure #4."

Response:

(1) We agree with the editor that it is not a normal atmospheric situation of the mimic reaction system. In fact, this phenomenon may exist in dusty weather. Some background had been mentioned in the section of Introduction of the manuscript: "*Atmospheric TiO_2 is mainly derived from windblown mineral dust, with mass mixing ratios ranging from 0.1 to 10% (Chen et al., Chem. Rev., 2012, 112, 5919-5948). TiO_2 is widely used in industrial processes and building exteriors for its favorable physical and chemical properties, and therefore the atmospheric TiO_2 content accumulates gradually. Titanium and nitrate ions have been found to coexist in atmospheric particulates in different regions worldwide (Sun et al., J. Geophys. Res. Atmos., 2005, 110, 1-11; Liu et al., AE, 2005, 39, 4453-4470; Yang et al., ACP, 2011, 11, 5207-5219; Kim et al., B. Korean Chem. Soc., 2012, 33, 3651-3656).*" Moreover, Sun et al. (J. Geophys. Res. Atmos., 2005, 110, 1-11) observed that the $NO_3^-/(NO_3^-+TiO_2)$ mass

percentage of total suspended particulate matter (TSP) during dust storms can be lower than 20%. We have added this result in the revised manuscript, see in Line 77-79. In this case, the NO_3^--TiO_2 composite particles with TiO_2 as the main body can in some extent represent the real situation under sandstorm weather and have some practical significance. Moreover, in cities with high traffic density, HCHO concentrations will be much higher than normal because of combustion emissions. 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; T. Salthammer, Build. Environ., 2019, 150, 219-232). This description of the presence of high HCHO concentration has been added in the Line 96-98 of revised manuscript.

(2) With regard to the Abstract, we rewrote it for better understanding by listing the experimental parameters, stating the limitation and clarifying the reaction pathway in the revised manuscript. The revised abstract is as follows with added or modified text marked in red: "Renoxification is the process of recycling of NO_3^-/HNO_3 into NO_x under illumination, which is mostly ascribed to the photolysis of nitrate. TiO_2, a typical mineral dust component, can play its photocatalytic role in "renoxification" process due to NO_3 radical formed, and we define this process as "photocatalytic renoxification". Formaldehyde (HCHO), the most abundant carbonyl compound in the atmosphere, may participate in the renoxification of nitrate-doped TiO_2 particles. In this study, we established a 400 L environmental chamber reaction system capable of controlling 0.8-70% relative humidity at 293K, with the presence of 1 or 9 ppm HCHO and 4 wt.% nitrate-doped TiO_2. The direct photolyses of both nitrate and NO_3 radical were excluded by adjusting the illumination wavelength, so as to explore the effect of HCHO on the "photocatalytic renoxification". It was found that NO_x concentration can reach up to more than 100 ppb for nitrate-doped TiO_2 particles, while almost no NO_x was generated in the absence of HCHO. Nitrate type, relative humidity and HCHO concentration were found to influence NO_x release. It was suggested that substantial amounts of NO_x were produced via the

NO_3^--$NO_3\cdot$-HNO_3-NO_x pathway, where TiO_2 worked for converting "NO_3^-" to "$NO_3\cdot$", HCHO participated in transformation of "$NO_3\cdot$" to "HNO_3" through hydrogen abstraction, and "HNO_3" photolysis answered for mass NOx release. So, HCHO played a significant role in this "photocatalytic renoxification" process. These results were found based on simplified mimics for atmospheric mineral dust under specific experimental conditions, which might deviate from the real situation, but illustrated a possible way of HCHO in influencing nitrate renoxification in the atmosphere. Our proposed reaction mechanism by which HCHO promotes photocatalytic renoxification is helpful for deeply understanding the atmospheric photochemical processes and nitrogen cycling, and could be considered for better fitting of atmospheric model simulations with field observations in some specific scenarios."

(3) In the revised manuscript, we have renumbered the fourth figure in the manuscript as "Figure 4".