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Comment on acp-2022-6

Anonymous Referee #2

Referee comment on "The positive effect of formaldehyde on the photocatalytic renoxification of nitrate on TiO₂ particles" by Yuhan Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-6-RC2>, 2022

Liu et al. investigated the possible renoxification processes occurring on TiO₂ particles and mineral dust particles in presence of adsorbed nitrate, or HNO₃, in presence of HCHO. They suggest that HCHO and TiO₂ have a significant synergistic effect on the photocatalytic renoxification via a NO₃-NO₃-HCHO-HNO₃-NO_x pathway, in which adsorbed HCHO may react with nitrate radicals through hydrogen abstraction to form HNO₃ on the surface, resulting an enhanced generation of NO_x.

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

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 bag, 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.

The main conclusion of this work is that adsorbed HCHO reacts with adsorbed nitrate radicals, promoting NO_x 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 TiO₂, 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?

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.

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?