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Interactive comment on "Importance of atmospheric aging in reactivity of mineral dust aerosol: a case study of heterogeneous reaction of gaseous hydrogen peroxide on processed mineral particles" by Y. Zhao et al.

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We gratefully thank you for the constructive comments and suggestions. Our point-topoint replies to the individual comments are as follows.

This paper reports an experimental study of the H_2O_2 heterogeneous interaction with Al_2O_3 surface. The uptake coefficient of H_2O_2 is determined as a function of relative humidity (RH) and surface concentration of nitrate or sulfite. Pretreatment of the alumina surfaces with HNO₃ and SO₂ is shown to affect the H_2O_2 uptake in a complex

C15520

way: increase or decrease of the uptake coefficient depending on the surface coverage and RH. Possible mechanisms of the H_2O_2 interaction with HNO₃ and SO₂ processed Al_2O_3 surface are discussed.

(Q1) I would limit my review to one major comment concerning the measurement of the uptake coefficient of H_2O_2 which was the main objective of this experimental study. In fact, the original experimental data allowing to understand how the uptake coefficient was measured and to judge the quality of the experimental results are not presented in the manuscript. In the revised version the authors should detail the experimental approach used and particularly the following issues should be addressed:

(A1) In the revised manuscript, we have detailed the experimental approach used and the following issues (see below).

(Q2) to indicate how the contact time between H_2O_2 and surface was calculated and if it was varied;

(A2) Figure 1 in the revised manuscript shows the schematic diagram of the experimental set-up that consists of three main parts: reactor, pumping and gas handling system, and H_2O_2 detection system. The reactor (length 15 cm, ID 3.3 cm) is a quartz tube with two infrared windows made of ZnSe. The α -Al₂O₃ and CaCO₃ samples, with typical mass of 15 mg and 23 mg respectively, were evenly placed on a 250-mesh stainless steel circular grid and slightly compressed to form solid coatings, which was then mounted in the center of the reactor. The reactant-containing synthetic air was introduced into the reactor at a constant rate of 400 sccm (corresponding to line speed 0.86 cm s⁻¹). The gas/particle interaction occurred as the trace gas passed through the grid coated with particles. Given the particle sample thickness of 0.14 mm, the contact time between trace gas and surface was estimated to be 0.02 s.

(Q3) to give an example of H_2O_2 consumption kinetics; to show original data from which uptake coefficient was determined; to show the experimental data on the dependence of the uptake coefficient on exposure time of the surface to H_2O_2 and to specify

which value of the uptake coefficient was really measured: the question is if the steady state for the uptake coefficient really exists and even if so, the timescale of the surface deactivation can be different under different RH and surface coatings;

(A3) In the present study, the loss of gas-phase H_2O_2 was measured as H_2O_2 containing airflow exited the reactor. Two kinds of measurements were carried out: one was in the presence of particles (to get total loss of gas-phase H_2O_2) and one in the absence of particles (to obtain the wall loss of H_2O_2). Figure 2 in the revised manuscript shows an example of H_2O_2 uptake kinetics by alumina particles at 45% RH and surface nitrate coverage of 3.4×10^{18} molecules m^{-2} . Some loss (less than 5%) of gas-phase H_2O_2 in the absence of particles on grid was observed within the first several min of exposure and then appeared to approach a constant value due to the surface saturation of the wall. By subtracting the wall loss from total loss of gas-phase H_2O_2 , the uptake of H_2O_2 by mineral particles can be derived. It can be seen that at the initial exposure stage, the uptake of H_2O_2 increase quickly and linearly, and after several min of exposure (> 10 min), the uptake rate seems to slow down due to the surface deactivation or saturation of particles. Similar phenomenon was observed for H_2O_2 uptake kinetics under other conditions (different RH and surface coating).

In this study, the uptake coefficients of H_2O_2 on processed particles were calculated using eqs (1) and (2) (see the revised manuscript). The uptake rate (d{C}/dt) of H_2O_2 was determined from the linear fit to the time-dependent uptake data within the first 10 min of exposure. It should be noted that although the timescale of the surface deactivation is different under different RH and surface coverage of coatings, a linear dependence of H_2O_2 uptake could be still observed with the first 10 min of exposure. However, the H_2O_2 uptake experiments in this work were performed at relative high H_2O_2 pressures, and on the timescale of several minutes the initial uptake processes may have already been achieved. Therefore, we think the measured uptake coefficients here may represent steady state but rather the initial state.

(Q4) to make and report error analysis on the measurements of the uptake coefficient.

C15522

(A4) In the present study, at least three individual experiments were averaged to get H_2O_2 uptake coefficients under each experimental condition. Errors are given as $\pm 1\sigma$, where σ is the standard deviation for individual measurements. The errors are mainly related to the repeatability of the surface coverage coating, stability of H_2O_2 gas-phase concentration, and accuracy of RH measurements.

The processing of mineral particles was performed independently in each experiment prior to H₂O₂ uptake, and the surface coverage coating is monitored using FTIR and determined using IC. The repeatability of the coverage for repeated experiments is within 10% on alumina and within 5% on CaCO₃. The concentration of gas-phase H₂O₂ was measured before and after each experiment and it remained constant to within 5% over the time of a kinetic run. The RH in airflow was measured at the outlet of the reactor using a commercial hygrometer (Vaisala HMT100) with an accuracy of ±1.7%.

(Q5) All these points concerning the measurements of the uptake coefficient are very important, especially when considering that all the effects observed in this study are relatively weak, not well pronounced. For example, all the data obtained for HNO₃ treated surfaces under different RH and with different surface coverage (Figure 3) can be described as $(0.8 \pm 0.3) \times 10^{-7}$, i.e. are similar within 35% uncertainty, which is realistic for this kind of measurements. Considering that the observed effects are rather weak, the experiments with higher (than 15% and 6%, respectively) coverage of nitrate and sulfite would be very useful to confirm the observed trends. Additional experiments with varied concentration of H₂O₂ would also be desirable.

(A5) It is reported that alumina is reactive insoluble and its reaction with HNO₃ is limited to the particle surface. Thus, the coverage of nitrate on HNO₃ treated alumina surfaces can not be very high, leading to a relatively weak effects on H_2O_2 uptake. Compared to alumina particles, CaCO₃ (calcite), as an important Ca-containing mineral dust in the atmosphere, is reactive soluble and especially reactive toward nitrogen oxides (Usher et al., 2003; Crowley et al., 2010). A number of field studies have observed a strong

correlation between dust nitrate and Ca²⁺ (Zhuang et al., 1999; Sullivan et al., 2007; Li et al., 2009). In particular, single particle studies have shown that Ca-containing mineral dust is frequently covered by visible Ca(NO₃)₂ coatings mainly through the reaction with HNO₃ (Kruegera et al., 2004; Li et al., 2009). Thus, the processed CaCO₃ appears to better represent the atmospheric mineral dust aged by reaction with HNO₃. In view of this, in the revised manuscript we have performed a number of additional experiments on HNO₃ treated CaCO₃ particles with varying coverage of nitrate (1–10 monolayer), as well as on SO₂ treated CaCO₃ surface with sulfite coverage of 50% monolayer, and we have observed far more pronounced effects on processed CaCO₃ particles (see details below). Besides, Additional experiments with varying concentration of H₂O₂ have also been conducted (also see details below). The results suggest that the uptake coefficients of H₂O₂ on HNO₃ and SO₂-processed particles appear to be independent of H₂O₂ concentration. This implies that the uptake behaviors of the processed mineral particles may be also applicable to lower H₂O₂ concentrations.

The results and discussion of H_2O_2 uptake on HNO_3 and SO_2 -processed CaCO₃ particles as well as H_2O_2 uptake at varying concentration of H_2O_2 have been added to the revised manuscript as seen in Sections 3.2.2, 3.3.2, and 3.4, and Fig. 6, Figs. 9 to12.

(Q6) In conclusion, although the manuscript seems to provide a new and interesting information, in my opinion, the work cannot be published in its present form and needs significant revision and, probably, additional experiments.

(A6) Thanks for your suggestion. In the revised manuscript, we have conducted a number of additional H_2O_2 uptake experiments including those on processed CaCO₃ particles and at varying H_2O_2 concentrations. Please see the details in (A5) and also in the revised manuscript.

Overall, by fully addressing all concerns both reviewers raised, we have made a significant revision for the manuscript. We believe that the revised manuscript is much improved.

C15524

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C15526