Atmos. Chem. Phys. Discuss., 10, C6065–C6068, 2010
www.atmos-chem-phys-discuss.net/10/C6065/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Irreversible loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid condensation" *by* R. C. Sullivan et al.

Anonymous Referee #1

Received and published: 4 August 2010

General comments

This experimental study investigates the effects of sulfuric acid condensation on the ice nucleation ability of ATD. Ice nucleation by mineral dust particles has attracted much interest recently. One open question is how aging of the mineral dust affects its ice nucleation ability. Sulfuric acid condensation is one type of aging that deserves consideration. This paper is well written. The experiments are in general well presented and the influence of the coating procedure on the ice nucleation ability of ATD is discussed in detail. One conclusion of this paper is that the way sulfuric acid and ammonium

sulfate coatings are deposited on the particles in the laboratory needs more consideration. During the coating process the particles are typically exposed to strongly acidic conditions and heat, both might lead to irreversible destruction of active sites. However, there is one issue, namely the limited timescale of the experiments that has not been given much attention in the discussion of the results. For conditions above water saturation, the particles are exposed to supersaturation for only few seconds. It is not clear whether this is long enough to dissolve the sulfuric acid coating. Active sites might regenerate on longer timescales. Such a discussion should be added to the revised manuscript.

One additional general comment concerns data evaluation: at the beginning of the results section, it is stated that changes in IN fraction do occur until ~105%, although above water saturation ice nucleation at the active sites should no longer respond to changes in the gas-phase relative humidity. Therefore, the frozen fraction at this value is taken to characterize immersion/condensation freezing. However, Figure 2 shows a plateau in IN fraction for the pure and the heated ATD at ~105% RHw but not for the SA treated ATD samples. For these samples the freezing onset seems to shift above water saturation. The frozen fraction increases continuously up to the limit for droplet break through, and the discrimination between evaporating droplets and ice crystals is less clear. Reasons for this should be discussed. As a consequence, evaluation at 108% RHw would increase the frozen fraction significantly and could affect some of the conclusions (e.g. the IN fraction of the sample SA 70C would be similar as the one of pure ATD). From the discussion of Fig. 2 (page 16913, lines 12-19) it does not become clear whether the authors postulate the presence of a plateau also for the SA treated samples. If yes, they should indicate it in the Figure.

Several parts of the discussion might improve when results of the ATOFMS results that were also performed during this study were included. E.g. variability of SA coatings between particles, formation of sulfate salts on the particle surface.

Specific comments

Page 16903, lines 19-20: why should conditions above water saturation be required for immersion freezing? Conditions at water saturation would be sufficient.

Page 16905, line 20: “The corona discharger did not change the IN ability”: Reference to Niedermeier et al. (2010) should be added to this statement.

Results section and Figure 2: readability of Figure 2 would improve if RHw for RHi = 100% at -30C were indicated. Also: RHi for RHw = 98% should be mentioned.

Fig. 3b: what is “ag” in “ag/particle”? A change to a mass fraction scale should be considered. This would allow a more direct comparison with the SA volume fraction from CCN shown in Fig. 3a.

Page 16914, line 21: “. . .responded similarly to all but one of the various physicochemical processing. . .”: It should be specified which one.

Pages 16921-22 and conclusions: The discussion of the effect of the water bath is confusing. The authors should be more explicit whether they think that the water bath had a direct effect on the IN fraction or whether the contamination with NH3 is responsible for the observed increase.

Pages 16923-16924: The comparison with previous studies should be extended. In addition to the studies mentioned by the authors, there are additional studies that did not show a decrease in heterogeneous ice nucleation ability by exposing ATD to sulfuric acid, namely Knopf and Koop (2006), who produced the SA coating from a dilute SA solution and Zobrist et al. (B. Zobrist, C. Marcolli, T. Peter, and T. Koop, Heterogeneous Ice Nucleation in Aqueous Solutions: the Role of Water Activity, J. Phys. Chem. A 2008, 112, 3965-3975), who investigated ATD particles immersed in sulfuric acid solutions. The only effect that Zobrist et al. observed was a freezing point depression due to the decreased water activity of the solution. Both studies suggest that sulfuric acid coatings of moderate concentration do not decrease the ice nucleation ability of ATD. Moreover, Niedermeier et al. (2010) only observed an effect of the SA coating

on the IN fraction for the highest temperature that they investigated, namely -34C. For lower temperatures coated and uncoated ATD behaved similarly.

Page 16924, lines 19-23: it is questionable whether the heterogeneous uptake of SO2 and subsequent oxidation to SA might lead to a concentrated SA coating, since ammonia is all the time available in the troposphere for immediate neutralization.

Page 16924, lines 26-28: Zobrist et al. (2008) have shown that ATD immersed in ammonium sulfate solutions showed no decrease in ice nucleation ability other than the freezing point depression expected due to the decreased water activity. This should be considered when discussing the effect of ammonium sulfate on immersion mode freezing of ATD.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 16901, 2010.