

Interactive comment on “Hygroscopic behavior of individual NaNO₃ particles” by M.-J. Lee et al.

M.-J. Lee et al.

curo@inha.ac.kr

Received and published: 31 October 2011

Reply to interactive comment on “Hygroscopic behavior of individual NaNO₃ particles” by M.-J. Lee et al.

Anonymous Referee #2

First of all, I thank the reviewer for his/her comments and review. And I appreciate his/her comments as they have very good points on our work. Please let me reply to the comments one by one.

1. comments: The main finding reported is that the hygroscopic response of substrate-deposited NaNO₃ particles depends on the preparation conditions – one “as received” powder particles and others obtained from a nebulizer. The difference is attributed to different nucleation mechanisms due to a possible presence of presumably insoluble

C11055

solids acting as a nucleation center for crystal growth. There are several concerns with this manuscript that I would like both authors and editor to carefully evaluate. 1) I find the finding in general useful to the community of researchers who measure hygroscopic properties of substrate-deposited particles that have atmospheric relevance. However, the present work is focused on a single type of particles (NaNO₃) and thus it is not clear how general is their observation – can similar effect present on other slats as well, for example? With this question in mind, I am not entirely convinced that ACPD is the best place to publish this work. If more particle types would be included to generalize the observed differences, it would justify publishing in this journal, largely due to the fact that there are many studies utilizing microscopy techniques to obtain water-uptake properties of submicrometer particles. 2) If more particle types would be included, and similar effect would be present, authors will need to partially rewrite their introduction to strengthen the atmospheric connection, otherwise it reads more like a technical paper specific to the particular experiment that was performed.

* reply: As comments 1 and 2 have related suggestions, I would like to reply to them together. Indeed, we already worked with “as received” powder particles and ones obtained from a nebulizer, collected on TEM grids, for NaCl, KCl, (NH₄)₂SO₄, Na₂SO₄, and KNO₃. Table 1 given in Supplement shows encountering probabilities for types 1-3 particles and their DRHs and ERHs for each inorganic compound, together with DRH and ERH values from other studies. For NaCl, KCl, (NH₄)₂SO₄, and Na₂SO₄, the homogeneous nucleation quickly occurs within measurement time scale, so that all the particles show clear DRHs and ERHs (type 3 particles). Our data of DRHs and ERHs for NaCl, KCl, (NH₄)₂SO₄, and Na₂SO₄ particles obtained by the nebulizer match well with those obtained by other studies. Also DRHs of dry deposited particles are consistent with DRHs of particles obtained by the nebulizer. However, ERHs of dry deposited particles are always higher than those of particles obtained by the nebulizer, indicating the presence of heterogeneous nucleation for dry deposited particles. KNO₃ particles showed similar hygroscopic behavior to that of NaNO₃ particles, where encountering probability of type 3 particles having clear DRHs and ERHs is 100% for dry deposited

C11056

particles and yet it is just 3.3% for particles obtained by the nebulizer. These results support our claims in our work for NaNO₃ particles. In addition, we investigated the hygroscopic properties of mixed NaCl/NaNO₃ particles with various compositions (in the range of 0.1 and 0.9 mole fractions of NaNO₃), which is under the preparation for a full paper. For NaNO₃-rich particles (mole fractions of NaNO₃ are higher than 0.74, i.e. eutonic composition of NaCl and NaNO₃ system) obtained by nebulization, just a phase transition for crystallization occurred during dehydration process. Our X-ray mapping measurement on those crystals of NaNO₃-rich particles indicated that they are composed of microcrystallines, for which a heterogeneous nucleation seems to be induced by NaCl. However, the particles containing a small amount of NaCl (less than 0.03 mole fraction of NaCl) underwent continuous growth and shrinkage without any phase transitions, similar to type 1 NaNO₃ aerosol particles. The results indicate that a sufficient amount of NaCl may be needed to induce the crystallization of NaNO₃-rich particles. These results for NaCl, KCl, (NH₄)₂SO₄, Na₂SO₄, KNO₃, and NaCl/NaNO₃ particles will be included in introduction and results and discussion parts of our revised version to somewhat generalize what we saw for NaNO₃ system.

2. comment: 3) Was there an attempt to identify the nature of crystal seeds? One could perform PXRD, mass-spec and TGA to get some additional experimental evidence on their presence. As it stands, the conclusion is highly hypothetical, although possible.

* reply: Two NaNO₃ powders purchased from Aldrich have 99.999% and 98% purities. As the chemical of 99.999% purity also seems to contain crystal germs, the concentration of the crystal germs should be less than 0.001%. I think that it is almost impossible for us to identify this trace amount of a chemical without any clue on its nature.

3. comment: 4) Minor comment regarding growth factor: the estimate does not take into account particle growth in the height and/or density, and hence has intrinsic error. While same is true for similar techniques like environmental SEM/TEM, a comment regarding this would be useful to include in the manuscript.

C11057

* reply: Regarding the particle growth factor, a specific word, "2D projected area ratio", will be used in our revised version, and the comment on why the specific word is used will include the points suggested by the reviewer.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C11055/2011/acpd-11-C11055-2011-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23203, 2011.

C11058