

Interactive comment on “Heterogeneous reactions of NO₂ with CaCO₃-(NH₄)₂SO₄ mixtures at different relative humidities” by Fang Tan et al.

Anonymous Referee #2

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General comments: The article aims to understand the uptake and kinetic behavior of a mixed aerosols system with its reaction with NO₂. The article has laid out all the aspects of the experiments and presented the data well. The role of (NH₄)₂SO₄ in the reaction was analyzed well. The data, summaries and mechanisms fits well but there are few major contradictory statements made in the different sections of the article that need clarification:

I recommend publication after a rewrite clarifying some of the major contradictory statement highlighted below:

Specific comments

The main issue I have is the role of (NH₄)₂SO₄ in the reaction. There seems to be two contradictory summaries being presented here, without explanation on how/why

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the $(\text{NH}_4)_2\text{SO}_4$ is causing these effects. There seems to be a cutoff RH value (60%), below which the effect of $(\text{NH}_4)_2\text{SO}_4$ is promotive and above which the effect is opposite (see page 10, line 26; page 12, line 3; page 13, line 19, or 21 ;). The authors have proposed active site dependence, (page 10, line 26) and deliquescence of $(\text{NH}_4)_2\text{SO}_4$ (page 14, line 16) as possible reasons for this. The way the sample mixture was made (page 5 line 21) contradicts the first reason; and these negative effect starts at 60% RH (which is further lower than DRH of $(\text{NH}_4)_2\text{SO}_4$ contradicts the second reason. The role of $(\text{NH}_4)_2\text{SO}_4$ is important (as the authors have clearly shown), their reasons for the observed effects need more explanations, and these contradictory statements do not help the reader/article.

Page 9, line 2-5: The identification of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ uses very similar IR peaks. It's not entirely clear how these same peaks were used to differentiate the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Page 9 line 21: How is the decomposition of CaCO_3 manifest itself as an increasing intensity of the 1570 cm^{-1} band? Decomposition usually leads to a negative (loss of) intensity, not a positive (increasing) intensity. The 1570 cm^{-1} has been assigned to HSO_4^- , how is the increasing intensity of this peak tie-in to the loss of CaCO_3 ? I am assuming it's from a specific reaction, but this is not clearly stated here.

Page 9 line 27: "...surface nitrate was decreased with increased $\text{Ca}(\text{NO}_3)_2$ content..". The sentence seems contradictory, how was the surface nitrate and bulk nitrate differentiated from the spectra?

Page 10 line 14-15: "...was faster than the reaction of..." how was this (fast reaction) determined? Needs more explanation.

Page 12, equation 2 and 3: Why are there two formulae for the calculation of reactive uptake coefficient? One uses $\text{dN}(\text{NO}_2)$ and the other uses dNO_3 ?

Page 14, line 1 : They report that the amorphous hydrate $\text{Ca}(\text{NO}_3)_2$ has weak inter-

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action with $(\text{NH}_4)_2\text{SO}_4$, but the following sentence (same page, line 5), they suggest that $\text{Ca}(\text{NO}_3)_2$ could interact with $(\text{NH}_4)_2\text{SO}_4$ to form NH_4NO_3 . How do they explain these contradictory statements?

Technical corrections:

Page 3 line 2: should be “gaseous”, not gases.

Page 3 line 8 : remove the “1” in front of “Pathak”.

Page 3 line 16: “. . .significant relevance”. Incomplete sentences, relevance to what?

Page 3, line 22: change “was” to “were”.

Page 3 line 26: “...after being exposed to. . .”.

Page 4 line 4: “. . .attributing it to. . .”.

Page 4 line 12: what do they mean by, “The catalysis and basic coexists could. . .”

Page 6 line 9: add “respectively” at the end of the sentence.

Page 7 line 7: How “dry” (< 1% humidity?) were the experimental conditions? It has been reported in literature that there are enough water layers at $\text{RH} < 5\%$ RH to influence surface reactions. Their “dry” experimental (RH) conditions should be presented.

Page 9 line 23: “. . .can be concluded. . .”

Page 10 line 1: “. . .add a comma after N_2 , its confusing without it.

Page 11, line 17: where are the “. . .stable formation” states/rates? This statement needs to be explained.

Page 12, line 10: create a better notation for the effective surface area, because “As” is confusing.

Page 13, line 29: remove “with absence of water vapor”. It’s redundant since you have

mentioned “under dry conditions” at the beginning of the sentence.

Page 14, line 9: “. . .decreased. . .”

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