Interactive comment on “Heterogeneous reactions of NO$_2$ with CaCO$_3$-(NH$_4$)$_2$SO$_4$ 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 NO$_2$. The article has laid out all the aspects of the experiments and presented the data well. The role of (NH$_4$)$_2$SO$_4$ 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 (NH$_4$)$_2$SO$_4$ in the reaction. There seems to be two contradictory summaries being presented here, without explanation on how/why
the (NH4)2SO4 is causing these effects. There seems to be a cutoff RH value (60%), below which the effect of (NH4)2SO4 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 (NH4)2SO4 (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 that DRH of (NH4)2SO4 contradicts the second reason. The role of (NH4)2SO4 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 CaSO4.0.5H2O and CaSO4.2H2O uses very similar IR peaks. It’s not entirely clear how these same peaks were used to differentiate the CaSO4.0.5H2O from the CaSO4.2H2O.

Page 9 line 21: How is the decomposition of CaCO3 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 HSO4-, how is the increasing intensity of this peak tie-in to the loss of CaCO3? 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 Ca(NO3)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 dN(NO2) and the other uses dNO3?

Page 14, line 1: They report that the amorphous hydrate Ca(NO3)2 has weak inter-
action with (NH4)2SO4, but the following sentence (same page, line 5), they suggest that Ca(NO3)2 could interact with (NH4)2SO4 to form NH4NO3. 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 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 N2, 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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