# Response

## Response to referee:

We are grateful to Referee #2 for giving valuable comments and helpful suggestions to improve our manuscript. Our response to the comments and changes to the manuscript are included below. We repeat the specific points raised by the reviewer in bold font, followed by our response in italic font. The manuscript that referee #2 commented is the version that delivered to Atmospheric Chemistry and Physics (ACP) initially, while we had made some small modifications according to the suggestions from Referee #1 in the ACPD version. The numbers of pages and lines are consistent with those in the ACPD paper to avoid misunderstanding.

**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 $(NH_4)_2SO_4$ 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:**

**Reply:** *We appreciate the reviewer's comments. And we have carefully revised our manuscript according to the reviewer's suggestions.*

**Specific comments**

**1. The main issue I have is the role of $(NH_4)_2SO_4$ in the reaction. There seems to be two contradictory summaries being presented here, without explanation on how/why the $(NH_4)_2SO_4$ is causing these effects. There seems to be a cutoff RH value (60%), below which the effect of $(NH_4)_2SO_4$ 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 $(NH_4)_2SO_4$ (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 that DRH of $(NH_4)_2SO_4$ contradicts the second reason. The role of $(NH_4)_2SO_4$ 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.**

***Reply:*** *Thanks for the reviewer's comment. We were regretful that we did not clarify enough about how $(NH_4)_2SO_4$ was causing effects in the heterogeneous reaction, resulting in misunderstanding of the reviewer and reader. In fact, we did not mention that active site dependence and the deliquescence of $(NH_4)_2SO_4$ were responsible for the effects of $(NH_4)_2SO_4$ in this paper. And 60% RH is not a cutoff RH between the two opposite effects.* ***We did emphasize that the chemical interaction of $(NH_4)_2SO_4$ with $Ca(NO_3)_2$ or $CaCO_3$ were the possible reasons for the promotive or inhibiting effects (page 10 line 1-19, page 13 line 12-14, page 13 line 27-29, page 14 line 1-15) and the nitrate concentrations were enhanced under all the wet conditions investigated (40%, 60% and 85% RH) (page 13 line 14-21 and line 23-25).***

*Firstly,* ***$(NH_4)_2SO_4$ has little effects on nitrate formation in the heterogeneous reaction of the mixtures with $NO_2$ under dry condition (page 13 line 27-29 and page 14 line 1).*** *Figure 1a indicated that $(NH_4)_2SO_4$ particles has limited interaction with the amorphous state $Ca(NO_3)_2$ and Figure 2 suggested that it has little reaction with $CaCO_3$ particles under dry condition. The reactive sites dependence was the possible reason to explain the results that the lasting time of initial stages and the $NO_3^-$ mass concentrations decrease linearly with increasing $(NH_4)_2SO_4$ content in the mixtures (as the reviewer mentioned, on page 10 line 27-28 in initial manuscript version), since the nitrate is produced from the uptake of $NO_2$ on $CaCO_3$ particles without the participation of $(NH_4)_2SO_4$ under dry condition.*

*As RH increased from dry condition to* ***40% RH, the chemical reaction of $CaCO_3$ with $(NH_4)_2SO_4$ particles is still neglectable (Figure 2). And the chemical interaction of the deliquesced $Ca(NO_3)_2$ with $(NH_4)_2SO_4$ particles are responsible for the formation of $NH_4NO_3$ and $CaSO_4$ $0.5H_2O$****, which may enhance the ionic* *mobility of the surface ions (Allen et al., 1996), modify the surface structure and re-expose reactive sites (Al-Hosney and Grassian, 2005), consequently showing promotive effects on the nitrate formation during the heterogeneous reaction of* $NO_2$ *with the mixtures.*

*At 60% RH,* ***a chemical reaction in the coagulation of*** $CaCO_3$ ***and*** $(NH_4)_2SO_4$ ***particles actually occurs without the introduction of*** $NO_2$ *(page 10 line 9-11). Consequently,* $CaCO_3$ *particles are partly consumed during the coagulation with* $(NH_4)_2SO_4$ *and the* $CaSO_4\ nH_2O$ *formed in the coagulation may block reactive sites for further reaction, resulting in an inhibiting effect on nitrate formation (page 14 line 9-15). At the same time, the deliquesced* $Ca(NO_3)_2$ *still has chemical interactions with* $(NH_4)_2SO_4$ *(page 10 line 13-19).* ***Therefore, there is a combined effect of the two opposing effects from the interaction of*** $(NH_4)_2SO_4$ ***with*** $Ca(NO_3)_2$ ***and the interaction of*** $(NH_4)_2SO_4$ ***with*** $CaCO_3$***.*** *Furthermore, it is well consistent with the results that the nitrate formation rates and the* $NO_3^-$ *mass concentrations at 60% RH are slightly larger than those at 40% RH for the mixtures with mass percentage of* $(NH_4)_2SO_4$ *smaller than 43%, while it is opposite for the mixtures with mass percentage of* $(NH_4)_2SO_4$ *larger than 57%.* ***Thus 60% RH is not a cutoff value.***

*As for 85% RH,* ***the deliquescence of*** $(NH_4)_2SO_4$ ***(Cziczo et al., 1997) leads to more water uptake on the mixture surfaces, facilitating the reaction of*** $(NH_4)_2SO_4$ ***with*** $CaCO_3$ ***(page 14 line15-16).*** *Therefore the negative effects are more obvious at 85% RH than at 60% and 40% RH. It should be noticed that although the nitrate formation rates and* $NO_3^-$ *mass concentrations at 85% RH are smaller than those at 60% and 40% RH, the nitrate concentrations are still improved at 85% RH (page 13 line 17-25).*

*Some modifications have been made in order to clarify clearly how* $(NH_4)_2SO_4$ *affects the nitrate formation in the heterogeneous reaction of* $NO_2$ *with* $CaCO_3$*-*$(NH_4)_2SO_4$ *mixtures at different RHs.*

***Related changes included in the revised manuscript:***

*Page 2 line 15-17: the sentence "Under wet conditions, the* $CaCO_3$*-*$(NH_4)_2SO_4$ *mixtures exhibited…." was revised to "Under wet conditions, the chemical interaction of* $(NH_4)_2SO_4$ *with* $Ca(NO_3)_2$ *has a promotive effects on the nitrate formation in the* *heterogeneous reaction of the mixtures with* $NO_2$*, while the coagulation of* $(NH_4)_2SO_4$ *with* $CaCO_3$ *exhibits an inhibiting effects at the same time. The nitrate formation is promoted in the heterogeneous reaction of* $NO_2$ *with* $CaCO_3$*-*$(NH_4)_2SO_4$ *mixtures, especially at medium RHs."*

*Page 10 line 7-9: the sentence "... therefore the heterogeneous reactions of* $NO_2$ *with the* $CaCO_3$*-*$(NH_4)_2SO_4$ *mixtures were responsible for the formation of bassanite." was revised to "... therefore the chemical interaction of* $Ca(NO_3)_2$ *with* $(NH_4)_2SO_4$ *was responsible for the formation of bassanite in these conditions."*

*Page 10 line 17-19: the sentence "And there were additional gypsum and koktaite products formed…." was revised to "Thus* $CaSO_4$ $nH_2O$ *and koktaite products could be formed both from the chemical interaction of* $(NH_4)_2SO_4$ *with* $Ca(NO_3)_2$ *and the reaction of* $(NH_4)_2SO_4$ *with* $CaCO_3$ *at 60% and 85% RH."*

*Page 11 line 22, after the sentence "…followed by that at 85% RH" we added "While for the mixtures with mass fraction of* $(NH_4)_2SO_4$ *smaller than 43%, the nitrate formation rates increased initially as RH elevated from 40% RH to 60% RH then it decreased obviously as RH increased to 85% RH. The differences in the tend of the nitrate formation rates with RH for the mixtures could be explained by the combined opposite effects from the interaction of* $(NH_4)_2SO_4$ *with* $Ca(NO_3)_2$ *or* $CaCO_3$ *at 60% RH."*

*Page 11 line 26, after the sentence "…at corresponding RH, respectively" we added "As RH increased from dry condition to 40% and 60% RH, the initial nitrate formation rates decreased less for the reaction of* $NO_2$ *with the mixtures than with* $CaCO_3$ *particles, while it was opposite as RH increased to 85% RH"*

*Page 13 line 17-18: before the sentence "The* $NO_3^-$ *mass concentrations for the mixture of FAS-57…" we added "The* $NO_3^-$ *mass concentrations increase much more for the mixtures than for pure* $CaCO_3$ *particles as RH elevated from dry condition to wet conditions, e.g."*

*Page 14 line 7: after the sentence "…*expose additional active sites on $CaCO_3$ *particles in the mixtures" we added "Thus the chemical interaction of* $Ca(NO_3)_2$ *and*

*$(NH_4)_2SO_4$ particles may exhibits promotive effects on the nitrate formation during the heterogeneous reaction of $NO_2$ with $CaCO_3$-$(NH_4)_2SO_4$ mixtures."*

*Page 14 line 7-9: the sentence "However, the nitrate formation rates and nitrate concentrations at 60% RH was decreased compared to those at 40% RH for the mixtures with mass percentage of $(NH_4)_2SO_4$ larger than 57%." was revised to "The nitrate formation rates and nitrate concentrations increase slightly when RH increased from 40% RH to 60% RH for the mixtures with mass percentage of $(NH_4)_2SO_4$ less than 43%. However, it was opposite for the mixtures with mass percentage of $(NH_4)_2SO_4$ larger than 57% that the nitrate formation rates and nitrate concentrations at 60% RH are smaller than those at 40% RH."*

*References:*

*Al-Abadleh, H. A., Al-Hosney, H. A., and Grassian, V. H.: Oxide and carbonate surfaces as environmental interfaces: the importance of water in surface composition and surface reactivity, J. Mol. Catal. A: Chem., 228, 47-54, doi:10.1016/j.molcata.2004.09.059, 2004.*

*Al-Hosney, H. A., and Grassian, V. H.: Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study, Phys. Chem. Chem. Phys., 7, 1266-1276, doi:10.1039/b417872f, 2005.*

*Allen, H. C., Laux, J. M., Vogt, R., Finlayson-Pitts, B. J., and Hemminger, J. C.: Water-induced reorganization of ultrathin nitrate films on NaCl: Implications for the tropospheric chemistry of sea salt particles, J. Phys. Chem., 100, 6371-6375, doi:10.1021/jp953675a, 1996.*

*Mori, I., Nishikawa, M., and Iwasaka, Y.: Chemical reaction during the coagulation of ammonium sulphate and mineral particles in the atmosphere, Sci. Tot. Environ., 224, 87-91, doi:10.1016/s0048-9697(98)00323-4, 1998.*

**2. Page 9, line 2-5: The identification of $CaSO_4.0.5H_2O$ and $CaSO_4.2H_2O$ uses very similar IR peaks. It's not entirely clear how these same peaks were used to differentiate the $CaSO_4.0.5H_2O$ from the $CaSO_4.2H_2O$.**

***Reply:*** *Thanks for the reviewer's comment. The IR absorption peaks at 1008 and 1116* *cm$^{-1}$ due to $CaSO_4.0.5H_2O$ and the peaks at 1005 and 1117 cm$^{-1}$ due to $CaSO_4.2H_2O$ are hard to distinguish. There are, actually, some features that can be used to differentiate $CaSO_4.0.5H_2O$ from $CaSO_4.2H_2O$. As has been described in this paper (page 9, line 6-9), the peaks at 1096 and 1155 cm$^{-1}$ belong to $CaSO_4.0.5H_2O$ can be clearly observed in the IR spectrum, which are evidences for the formation of $CaSO_4.0.5H_2O$ rather than $CaSO_4.2H_2O$. Besides, $CaSO_4.2H_2O$ shows two IR-active modes in the bending modes of crystal hydrate water at 1620 and 1685 cm$^{-1}$, while $CaSO_4.0.5H_2O$ has only one band at 1620 cm$^{-1}$. Furthermore, the two stretching modes of crystal hydrate water occur at 3495, 3545 and 3400 cm$^{-1}$ for $CaSO_4.2H_2O$, at 3555 and 3610 cm$^{-1}$ for $CaSO_4.0.5H_2O$ (Prasad, 2005; Liu et al., 2009).*

***Related changes included in the revised manuscript:***

*Page 9 line 4-6: the sentence "The IR absorption bands of ..." was revised to "Although the IR absorption bands of bassanite and gypsum had some overlaps in the region between 1000 and 1250 cm$^{-1}$, there were some features that could be used to differentiate $CaSO_4.0.5H_2O$ from $CaSO_4.2H_2O$."*

*References:*

*Liu, Y., Wang, A., Freeman, J. J.: Raman, Mir, and NIR spectroscopic study of calcium sulfates: gypsum,bassanite, and anhydrite, 40th Lunar and Planetary Science Conference, 2009.*

*Prasad, P. S. R., Krishna Chaitanya, V., Shiva Prasad, K., and Narayana Rao, D.: Direct formation of the γ-$CaSO_4$ phase in dehydration process of gypsum: In situ FTIR study, Am. Mineral., 90, 672-678, doi:10.2138/am.2005.1742, 2005.*

**3. 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 $HSO_4^-$, 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.**

***Reply:*** *Thanks for the reviewer's suggestions. Normally, the decomposition of* *reactants leads to a negative intensity of IR spectrum in DRIFTS experiments.* ***In this study, the IR absorption peak at 1570 cm$^{-1}$ is assigned to the asymmetric stretching of $HCO_3^-$*** *(Al-Hosney et al., 2004; Li et al., 2010). In fact, there is no interruption from the IR absorption bands of other reactants and products in this range.* ***The positive intensity is likely due to the increasing information of $HCO_3^-$, which is from the decomposition of bulk $CaCO_3$ under wet conditions.*** *As indicated in Figure 1, the peak at 1570 cm$^{-1}$ did not appear under dry condition and it increased with increasing RH. The reactions are limited to surfaces and $H_2CO_3$ can exist as absorbed phase under dry condition. While the reaction of $NO_2$ can occur not only on the surfaces of $CaCO_3$ and mixtures but also into the bulk of the samples in the presence of surface condensed water (Goodman et al., 2001; Goodman et al., 2000). Furthermore, the acidity of surface condensed water is enhanced as a result of the formation of $HNO_3$ and the dissolution of $(NH_4)_2SO_4$, which facilitates the decomposition of the bulk $CaCO_3$ particles.*

***Related changes included in the revised manuscript:***

*Page 9 line 23-24: the sentence "Additionally, the increasing intensity of absorption bands at 1570 cm$^{-1}$ implied that the decomposition of $CaCO_3$ was enhanced at 85% RH." was revised to "Additionally, the IR absorption peaks at 1570 cm$^{-1}$ in Figure 1d were much stronger than those at 40% and 60% RH. The positive intensity was likely due to the increasing information of $HCO_3^-$, which was from the decomposition of the bulk $CaCO_3$ under wet conditions. It could be interpreted that the reaction of $NO_2$ can occur not only on the surfaces of $CaCO_3$ and the mixtures but also into the bulk of the samples under wet conditions. Also the acidity of surface condensed water was enhanced as a result of the formation of $HNO_3$ and the dissolution of $(NH_4)_2SO_4$, which facilitates the decomposition of bulk $CaCO_3$ particles."*

***References:***

*Al-Hosney, H. A., and Grassian, V. H.: Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study, Phys. Chem. Chem. Phys., 7, 1266-1276, doi:10.1039/b417872f, 2005.*

*Al-Hosney, H. A., and Grassian, V. H.: Carbonic Acid: an important intermediate in the surface chemistry of calcium carbonate, J. Am. Chem. Soc., 126, 8068-8069, doi:10.1021/ja0490774, 2004.*

*Goodman, A. L., Bernard, E. T., and Grassian, V. H.: Spectroscopic study of nitric acid and water adsorption on oxide particles: Enhanced nitric acid uptake kinetics in the presence of adsorbed water, J. Phys. Chem. A, 105, 6443-6457, doi:10.1021/jp003722l, 2001.*

*Goodman, A. L., Underwood, G. M., and Grassian, V. H.: A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles, J. Geophys. Res., 105, 29053-29064, doi:10.1029/2000jd900396, 2000.*

*Li, H. J., Zhu, T., Zhao, D. F., Zhang, Z. F., and Chen, Z. M. : Kinetics and mechanisms of heterogeneous reaction of* $NO_2$ *on* $CaCO_3$ *surfaces under dry and wet conditions, Atmos. Chem. Phys., 10, 463–474, 2010.*

**4. Page 9 line 27: "…surface nitrate was decreased with increased** $Ca(NO_3)_2$ **content..". The sentence seems contradictory, how was the surface nitrate and bulk nitrate differentiated from the spectra?**

***Reply:*** *Thanks for the reviewer's advice. This sentence should be corrected to "Moreover, the surface nitrate was decreased with increasing* $(NH_4)_2SO_4$ *content in mixtures." (page 9 line 27-28). This sentence was in the initial manuscript and it had been deleted in the ACPD version. I think it cannot differentiate surface nitrate from bulk nitrate according to IR spectra.*

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

***Reply:*** *Thanks for the reviewer's advice. We realized that the sentence "This is likely due to the fact that the reaction between* $(NH_4)_2SO_4$ *and* $Ca(NO_3)_2$ *was faster than the reaction of* $(NH_4)_2SO_4$ *with* $CaCO_3$*." was misleading. What we wanted to express was that* $Ca(NO_3)_2$ *were more hygroscopic and soluble than* $CaCO_3$ *and it may has stronger chemical interaction with* $(NH_4)_2SO_4$ *than* $CaCO_3$ *particles under the same condition.*

*This sentence was in the initial manuscript and it had been deleted in the ACPD version.*

***Related changes included in the revised manuscript:***

*Page 10 line 9: before the sentence "Furthermore, absorption bands ..." we added "This is likely due to the fact that* $Ca(NO_3)_2$ *is more hygroscopic and soluble than* $CaCO_3$ *particles."*

**6. 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?**

***Reply:*** *Thanks for the reviewer's comments. In the equation 2 and 3,* $N(NO_2)$ *is the number of reactive* $NO_2$ *collisions with the surface and* $\{NO_3\}$ *is surface concentrations of the nitrate.* $dN(NO_2)/dt$ *represents the rate of the reactive collisions with the surface and* $d\{NO_3\}/dt$ *means the nitrate formation rate. The reactive uptake coefficient (*$\gamma$*) is defined as the rate of the reactive collisions with the surface divided by the total number of surface collisions per unit time (Z) as expressed in equation 2. In the reaction of* $NO_2$ *with* $CaCO_3$ *particles and* $(NH_4)_2SO_4$*-*$CaCO_3$ *mixtures, the reactive* $NO_2$ *collisions with the surface lead to the formation of* $NO_3^-$*. Thus the rate of the reactive* $NO_2$ *collisions with the surface can be quantified in terms of the nitrate formation rate (Börensen et al., 2000; Li et al., 2006; Tong et al., 2010; Ullerstam et al., 2002).*

***Related changes included in the revised manuscript:***

*Page 12 line 14-15: the sentence "The rate of reactive collision can be obtained from the nitrate formation rate* $d\{NO_3^-\}/dt$*, ..." was revised to "The rate of reactive* $NO_2$ *collision with the surface can be quantified in terms of the nitrate formation rate* $d\{NO_3^-\}/dt$*, ..."*

***References:***

*Börensen, C., Kirchner, U., Scheer, V., Vogt, R., and Zellner, R.: Mechanism and kinetics of the reactions of* $NO_2$ *or* $HNO_3$ *with alumina as a mineral dust model compound, J. Phys. Chem. A, 104, 5036-5045, doi:10.1021/jp994170d, 2000.*

*Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, Atmos. Chem. Phys., 6, 2453–2464, 2006.*

*Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on* $\alpha$*-*$Al_2O_3$ *at different relative humidities, Atmos. Chem. Phys., 10, 7561-7574, doi:10.5194/acp-10-7561-2010, 2010.*

*Ullerstam, M., Vogt, R., Langer, S., and Ljungstrom, E.: The kinetics and mechanism of* $SO_2$ *oxidation by* $O_3$ *on mineral dust, Phys. Chem. Chem. Phys., 4, 4694-4699, doi:10.1039/b203529b, 2002.*

**7. 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?**

***Reply:*** *Thanks for the reviewer's comments. It was reported that* $Ca(NO_3)_2$ *was in the state of amorphous state at RH < 7% and solution droplets at RH > 10%. In this study, the* $Ca(NO_3)_2$ *was in the state of amorphous state under dry condition and solution droplets at 40% RH (page 8 line 10-14). Also the chemical interaction of* $Ca(NO_3)_2$ *with* $(NH_4)_2SO_4$ *is responsible for the formation of* $CaSO_4\ 0.5H_2O$ *under dry condition and 40% RH. Figure 1a indicates that the IR absorption bands of* $CaSO_4\ 0.5H_2O$ *are weak under dry condition (the vibration modes of water group in* $CaSO_4\ 0.5H_2O$ *are too weak to be identified), while the IR peaks of* $CaSO_4\ 0.5H_2O$ *can be clearly observed at 40% RH (Figure 1b). The results indicate that the chemical interaction of* $Ca(NO_3)_2$ *with* $(NH_4)_2SO_4$ *is enhanced with the deliquescence of* $Ca(NO_3)_2$*. The possible reasons are that the deliquesced* $Ca(NO_3)_2$ *leads to more water uptake on the mixture surfaces and that the ionic mobility of the surface ions are improved in solution droplets.*

***Related changes included in the revised manuscript:***

*The sentence "Meanwhile, the deliquesced* $Ca(NO_3)_2$ *could interact with* $(NH_4)_2SO_4$

*particles to form microcrystallites of* $NH_4NO_3$ *and* $CaSO_4\ nH_2O$*, …"on page 14 line 3-4 was revised to "Meanwhile, the chemical interaction of* $Ca(NO_3)_2$ *with* $(NH_4)_2SO_4$ *is enhanced with the deliquescence of* $Ca(NO_3)_2$*, resulting in the formation of microcrystallites of* $NH_4NO_3$ *and* $CaSO_4\ nH_2O$*."*

**Technical corrections:**

**8. Page 3 line 2: should be "gaseous", not gases.**

***Reply:*** *Page 3 line 2: "gases" was revised to "gaseous".*

**9. Page 3 line 8: remove the "1" in front of "Pathak".**

***Reply:*** *Page 3 line 8: "Pathakl" was revised to "Pathak".*

**10. Page 3 line 16: "··· significant relevance". Incomplete sentences, relevance to what?**

***Reply:*** *Page 3 line 15: the sentence "··· to explain the significant relevance." was revised to "··· to explain these phenomena."*

**11. Page 3 line 22: change "was" to "were".**

***Reply:*** *We revised "was" to "were" on page 3 line 20 in the sentence "Modeling studies indicated that mineral aerosols were highly associated with nitrate formation in the atmosphere."*

**12. Page 3 line 26: "... after being exposed to…".**

***Reply:*** *We revised "... after being exposed to ..." on page 3 line 24: "Calcium carbonate particle is converted to calcium nitrate after reaction with nitrogen oxides and* $HNO_3$ *in the atmosphere"*

**13. Page 4 line 4: "...attributing it to...".**

***Reply:*** *Thanks for the reviewer's comments. We revised the sentence "... attributing* *to the interaction of ions under humid condition." to "... as a result of the interaction of ions under humid condition."*

**14. Page 4 line 12: what do they mean by, "The catalysis and basic coexists could ..."**

***Reply:*** *Thanks for the reviewer's comments. The original sentence in the paper of Li et al. is "The catalytic and basic additives could enhance the production of sulfate on the NaCl surface." Their results showed that the additive of basic additives (e.g. MgO and $CaCO_3$) could greatly increase the basic property of the surface of NaCl and that $SO_2$ could easily absorbe on the alkaline surface and subsequently be oxidized into sulfate by $O_3$.*

***Related changes included in the revised manuscript:***

*The sentence "The catalysis and basic coexists could increase the formation of sulfate on NaCl particle surfaces." on page 4 line 10-11 was revised to "The catalytic and basic additives, e.g., MgO and $CaCO_3$, could increase the basic property of the surface of NaCl and increase the formation of sulfate by facilitating the absorbance of $SO_2$ on the alkaline surface."*

**15. Page 6 line 9: add "respectively" at the end of the sentence.**

***Reply:*** *We are thankful for this comment. We had added "respectively" at the end of the sentence on page 6 line 5-8 in the ACPD version.*

**16. 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.**

***Reply:*** *Thanks for the reviewer's comment. Dry condition represents an experiment condition that the gases entering reactor chamber with a very low relative humidity (RH). In this study, the condition when the gases are dehumidified by silica gel and* *molecular sieve to less than 1% RH before flowing into DRIFTs reactor chamber is called dry condition (page 5 line 28; page 6 line 1). The RH and temperature of the inflow of sample cell are measured using a commercial humidity and temperature sensor (HMT330; Vaisala) with a measurement accuracy of ±1% RH and ±0.2°C, respectively (page 6, line 6-8).*

*"Dry condition", actually, is widely used to describe a very low RH experiment condition in scientific papers. Goodman et al. (2000, 2001) used "dry condition" and "conditions near 0 relative humidity" in their papers. Al-Abadleh et al. (2004) described their experiment conditions as "under dry (<1% RH) and wet (20-25%) conditions". Also, Al-Hosney et al. (2005) described the condition as "under dry conditions near 0% RH", Li et al. (2010) described it as "dry condition (RH<10%)", and Tong et al. (2010) used "dry condition RH<1%".*

***References:***

*Al-Abadleh, H. A., Al-Hosney, H. A., and Grassian, V. H.: Oxide and carbonate surfaces as environmental interfaces: the importance of water in surface composition and surface reactivity, J. Mol. Catal. A: Chem., 228, 47-54, doi:10.1016/j.molcata.2004.09.059, 2004.*

*Al-Hosney, H. A., and Grassian, V. H.: Water, sulfur dioxide and nitric acid adsorption on calcium carbonate: A transmission and ATR-FTIR study, Phys. Chem. Chem. Phys., 7, 1266-1276, doi:10.1039/b417872f, 2005.*

*Goodman, A. L., Bernard, E. T., and Grassian, V. H.: Spectroscopic study of nitric acid and water adsorption on oxide particles: Enhanced nitric acid uptake kinetics in the presence of adsorbed water, J. Phys. Chem. A, 105, 6443-6457, doi:10.1021/jp003722l, 2001.*

*Goodman, A. L., Underwood, G. M., and Grassian, V. H.: A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles, J. Geophys. Res., 105, 29053-29064, doi:10.1029/2000jd900396, 2000.*

*Li, H. J., Zhu, T., Zhao, D. F., Zhang, Z. F., and Chen, Z. M. : Kinetics and mechanisms of heterogeneous reaction of $NO_2$ on $CaCO_3$ surfaces under dry and wet conditions, Atmos. Chem. Phys., 10, 463–474, 2010.*

*Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on α-*$Al_2O_3$ *at different relative humidities, Atmos. Chem. Phys., 10, 7561-7574, doi:10.5194/acp-10-7561-2010, 2010.*

*Ullerstam, M., Vogt, R., Langer, S., and Ljungstrom, E.: The kinetics and mechanism of* $SO_2$ *oxidation by* $O_3$ *on mineral dust, Phys. Chem. Chem. Phys., 4, 4694-4699, doi:10.1039/b203529b, 2002.*

**17. Page 9 line 23: "…can be concluded…"**

***Reply:*** *Thanks for the reviewer's comment. We revised the sentence "In addition, it can be concluded from Fig. 1 that* $NO_2$ *did not show…" on page 9 line 25 to "In conclusion,* $NO_2$ *did not show…"*

**18. Page 10 line 1: "…add a comma after N2, its confusing without it.**

***Reply:*** *Thanks for the reviewer's comment. We revised the sentence "In another set of experiments, the mixture of FAS-57 was exposed to nitrogen with corresponding RHs to investigate …" on page 10 line 1-2 to "In another set of experiments, the mixture of FAS-57 was exposed to nitrogen, with corresponding RHs in order to investigate …".*

**19. Page 11, line 17: where are the "… stable formation" states/rates? This statement needs to be explained.**

***Reply:*** *We are thankful for the reviewer's comment. Figure 3a represents the integrated absorbance of nitrate as a function of time under dry condition. It suggests that the formation of nitrate on* $CaCO_3$ *and the* $CaCO_3$*-*$(NH_4)_2SO_4$ *mixtures surfaces can be divided into three stages. Stage 1: the integrated absorbance of nitrate increases linearly with time and it is called initial stage. In this stage, the nitrate formation rate on particle surfaces is faster than in the other two stages. Stage 2 (transition stage): the increase of the integrated absorbance of nitrate slowed down. Stage 3: the integrated absorbance of nitrate increase at a relatively stable rate that is much smaller than that at stage 1 (Wu et al., 2013; Li et al., 2006; Li et al. 2010)*

***Related changes included in the revised manuscript:***

*We revised the sentence "The nitrate formation rates were fast at initial stage and then slowed down after a transition stage under dry condition." on page 10 line 25-26 to "The formation of nitrate on sample surfaces could be divided into three stages under dry conditions. The integrated absorbance of nitrate increased linearly with time in initial stage and it finally increase at a stable rate after a transition period."*

***References:***

*Li, H. J., Zhu, T., Zhao, D. F., Zhang, Z. F., and Chen, Z. M. : Kinetics and mechanisms of heterogeneous reaction of* $NO_2$ *on* $CaCO_3$ *surfaces under dry and wet conditions, Atmos. Chem. Phys., 10, 463–474, 2010.*

*Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, Atmos. Chem. Phys., 6, 2453–2464, 2006.*

*Wu, L. Y., Tong, S. R., and Ge, M. F.: Heterogeneous reaction of* $NO_2$ *on* $Al_2O_3$*: the effect of temperature on the nitrite and nitrate formation, J. Phys. Chem. A, 117, 4937-4944, doi:10.1021/jp402773c, 2013.*

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

***Reply:*** *We appreciate for the reviewer's comment. We agree that "As" is a little confusing in the sentence "Where N(*$NO_2$*) is the number of reactive* $NO_2$ *collisions with the surface, As is the effective surface area of samples and [*$NO_2$*] is the gas-phase concentration of* $NO_2$*" on page 12 line 11-12. We revised "As" to "*$A_{surface}$*" to avoid confusion (Ullerstam et al., 2002).*

***References:***

*Ullerstam, M., Vogt, R., Langer, S., and Ljungstrom, E.: The kinetics and mechanism of* $SO_2$ *oxidation by* $O_3$ *on mineral dust, Phys. Chem. Chem. Phys., 4, 4694-4699, doi:10.1039/b203529b, 2002.*

**21. 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.**

***Reply:*** *We deleted “with the absence of water vapor” in the sentence “Under dry condition, little reaction occurs between* $CaCO_3$ *and* $(NH_4)_2SO_4$*.” on page 13 line 27-28.*

**22. Page 14, line 9: “…decreased…”**

***Reply:*** *We had revised “decrease” to “decreased” in the sentence “However, the nitrate formation rates and nitrate concentrations at 60% RH decreased compared to those at 40% RH for the mixtures with mass percentage of* $(NH_4)_2SO_4$ *larger than 57%.” on page 14, line 7-9.*