

Response

Response to referee #1:

We are grateful to Referee #1 for the comments and the constructive 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 pages numbers and lines mentioned below are consistent with those in the Atmospheric Chemistry and Physics Discussions (ACPD) paper.

Mineral dust and sulfate are common components in atmospheric particulate matters (PMs), and their coagulation in the atmosphere can form new types of PMs whose physical and chemical characters will be altered, thus affecting on atmospheric physical and chemical processes. Because only few studies investigated the heterogeneous reactions under complex conditions, there is still large gap to explain many phenomena of field measurements by using the current knowledge of atmospheric chemistry. The new finding in this study about the heterogeneous reactions of NO_2 on the surface of $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures provided important information, that is, the heterogeneous reactions in the atmosphere may play important role on formation of nitrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (bassanite), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) and $(\text{NH}_4)_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$ (koktaite). This reviewer recommends the manuscript be published in the journal after considering the following one specific: The formation rates of nitrate based on the integrated absorbance of the IR peak area between 1390 and 1250 cm^{-1} are inconsistent with the final concentrations of nitrate measured by IC. The intensity of the IR absorbance in the DRIFTS can only reveal the surface concentration of nitrate, whereas the nitrate concentrations measured by IC are the bulk concentrations in the PMs. The surface nitrate formed through the heterogeneous reactions was suspected to easily diffuse into inner layer of the PMs under high RH conditions. The authors should present the explanations.

Reply: Thanks for the reviewer's comment. We agree with the reviewer's point that the

infrared beam primarily interrogates the upper portion of the particulate samples and IR absorbance in the DRIFTS reveals the surface concentration of nitrate. The infrared beam is, however, not restricted solely to the top few particle layers (Vogt and Finlaysonpitts, 1994). In fact, DRIFTS has been applied extensively to study the kinetics and mechanisms of gas-solid reactions (Ullerstam et al., 2002, 2003; Li et al., 2007; Li et al., 2010; Tong et al. 2010), where the kinetics of the reactions are followed using the integrated absorbance-reaction time behavior and the reactive uptake coefficient (γ) is determined from the infrared absorbance, that calibrated by ion chromatography (IC).

Vogt et al. (1994) investigated the depth of the pellet from which the infrared signal generated. They mixed homogeneous NaNO_3 or NaCl mixture with an additional 0.2-0.5mm layers of neat NaCl powder on top and found that significant signals could still be observed. Also they reported that the absorbance integrated over the ν_3 region was linearly dependent on the amount of nitrate determined by IC in the reaction of solid NaCl with gaseous NO_2 and HNO_3 . In this study, as indicated in Figure S3 that over a large concentration range the integrated nitrate absorbance over the ν_3 region (1390 to 1250 cm^{-1}) was proportional to the nitrate ions concentration detected by IC. In another word, the reacted particles were within the depth that infrared signal generated and the nitrate formed during the reaction could be presented by the integrated absorbance over the ν_3 region.

Li et al. (2010) investigated the heterogeneous reaction of CaCO_3 with NO_2 using a DRIFTS reactor and found that there was a linear relationship between absorbance integrated over the ν_1 region (1013 - 1073 cm^{-1}) and the number of nitrate ions determined by IC. They reported that the conversion factor f (in the equation of the nitrate ions $\{\text{NO}_3^-\} = (\text{integrated absorbance } I_A) \times f$) was found to be independent of reaction time and NO_2 concentration as long as the experiment was completed at a stage when the absorption of the nitrate band was still growing. In this research, we found that the integrated nitrate absorbance over the ν_1 region (1013 - 1073 cm^{-1}) and the ν_3 region (1250 - 1390 cm^{-1}) could well overlap after the former multiplied by a constant (see in Figure S2). And all the experiments in our study were completed as the integrated nitrate absorptions were still growing (Figure 3).

Therefore the nitrate formation rates based on the integrated absorbance of the IR peak area

between 1390-1250 were well consistent with the nitrate concentrations measured by IC.

Following the referee's suggestion, we added a series of experiments that stopped the heterogeneous reactions of NO_2 with CaCO_3 and $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures at the initial stage (e.g. 20min, 30min, and 40min) under wet and dry conditions. The results indicated that the integrated absorbance of nitrate has a linear relationship with the amount of nitrate determined by ion chromatography during all the reaction periods. Some modifications have been made in Figure S3 after some data added to the calibration plot. Figure S2 was added to illustrate that the integrated nitrate absorbance over the ν_1 region (1013-1073 cm^{-1}) and the ν_3 region (1250-1390 cm^{-1}) could well overlap after the former multiplied by a constant.

Related changes included in the revised manuscript:

Page 10 line 24, after the sentence "... interruption of the absorptions of sulfates" we added "The integrated nitrate absorbance over the ν_1 region (1013-1073 cm^{-1}) and the ν_3 region (1250-1390 cm^{-1}) could well overlap after the former multiplied by a constant (Figure S2)."

Page 11 line 12, we revised "Fig. S2" in the sentence "... at 60%, 40% RH and dry condition (see Fig. S2)." to Fig S3.

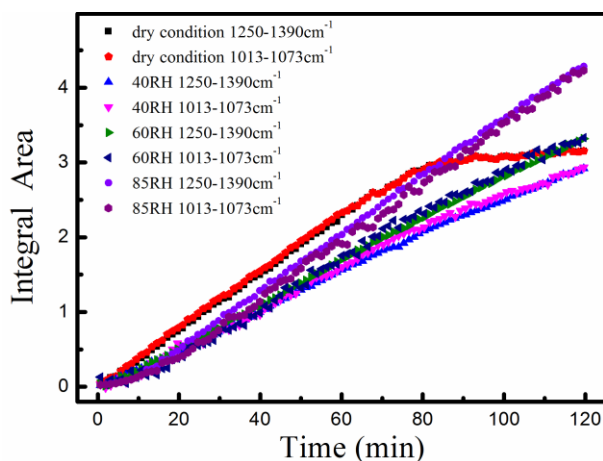


Figure S2: The integrated nitrate absorbance over the ν_1 region ($1013\text{--}1073\text{ cm}^{-1}$) and the ν_3 region ($1250\text{--}1390\text{ cm}^{-1}$) after the ν_1 region multiplied by 3, 7, 10, 12 under dry condition, 40% RH, 60% RH, and 85% RH, respectively, for the reaction of NO_2 with CaCO_3 particles.

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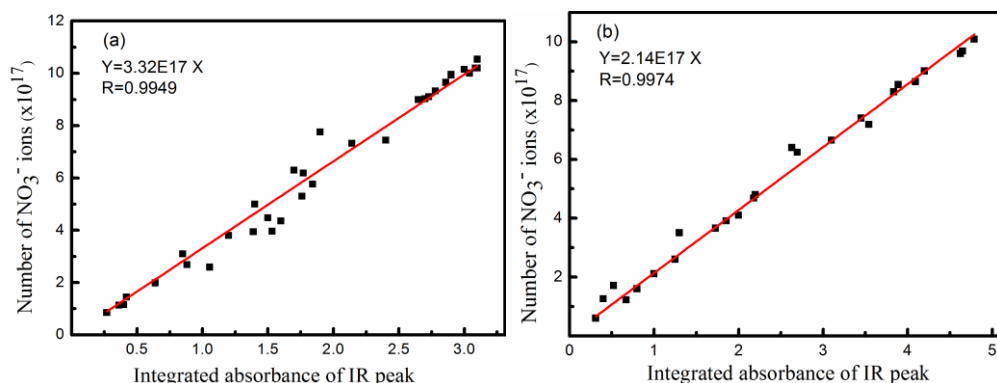


Figure S3. The number of NO_3^- ions detected by IC as a function of integrated absorbance of IR peak between 1390 and 1250 cm^{-1} at (a) dry condition, 40% RH, and 60% RH, (b) 85% RH.

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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.

15 Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, S., Li, H. J., Zhu, L. H., and Xu, B. Y.: Heterogeneous oxidation of sulfur dioxide by ozone on the surface of sodium chloride and its mixtures with other components, *J. Geophys. Res.-Atmos.*, 112,

doi:10.1029/2006jd008207, 2007.

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.

- 5 Liu, Y. J., Zhu, T., Zhao, D. F., and Zhang, Z. F.: Investigation of the hygroscopic properties of $\text{Ca}(\text{NO}_3)_2$ and internally mixed $\text{Ca}(\text{NO}_3)_2/\text{CaCO}_3$ particles by micro-Raman spectrometry, *Atmos. Chem. Phys.*, 8, 7205–7215, 2008.

- Tang, I. N., and Fung, K. H.: Hydration and Raman scattering studies of levitated microparticles: $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Ca}(\text{NO}_3)_2$, *J. Chem. Phys.*, 106, 1653–1660, doi:10.1063/1.473318, 1997.

- 10 Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on $\alpha\text{-Al}_2\text{O}_3$ 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.

- 15 Ullerstam, M., Johnson, M. S., Vogt, R., and Ljungstrom, E.: DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust, *Atmos. Chem. Phys.*, 3, 2043–2051, 2003.

- 20 Vogt, R., and Finlaysonpitts, B. J.: A Diffuse Reflectance Infrared Fourier-Transform Spectroscopic (DRIFTS) study of the surface-reaction of NaCl with gaseous NO_2 and HNO_3 , *J. Phys. Chem.*, 98, 3747–3755, doi:10.1021/j100065a033, 1994.

- 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.

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Response to referee #2:

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 $(\text{NH}_4)_2\text{SO}_4$ 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:

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 $(\text{NH}_4)_2\text{SO}_4$ in the reaction. There seems to be two contradictory summaries being presented here, without explanation on how/why 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.

Reply: Thanks for the reviewer's comment. We were regretful that we did not clarify enough about how $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ were responsible for the effects of $(\text{NH}_4)_2\text{SO}_4$ in this paper. And 60% RH is not a cutoff RH between the two opposite effects. We did emphasize that the chemical interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ 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, $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ particles have limited interaction with the amorphous state $\text{Ca}(\text{NO}_3)_2$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ under dry condition.

As RH increased from dry condition to 40% RH, the chemical reaction of CaCO_3 with $(\text{NH}_4)_2\text{SO}_4$ particles is still neglectable (Figure 2). And the chemical interaction of the deliquesced $\text{Ca}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ particles are responsible for the formation of NH_4NO_3 and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ and the $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ 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 $\text{Ca}(\text{NO}_3)_2$ still has chemical interactions with $(\text{NH}_4)_2\text{SO}_4$ (page 10 line 13-19). **Therefore, there is a combined effect of the two opposing effects from the interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ and the interaction of $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ smaller than 43%, while it is opposite for the mixtures with mass percentage of $(\text{NH}_4)_2\text{SO}_4$ larger than 57%. **Thus 60% RH is not a cutoff value.**

As for 85% RH, the deliquescence of $(\text{NH}_4)_2\text{SO}_4$ (Cziczo et al., 1997) leads to more water uptake on the mixture surfaces, facilitating the reaction of $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ affects the nitrate formation in the heterogeneous reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures at different RHs.

Related changes included in the revised manuscript:

Page 2 line 15-17: the sentence “Under wet conditions, the CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures exhibited....” was revised to “Under wet conditions, the chemical interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ has a promotive effects on the nitrate formation in the heterogeneous reaction of the mixtures with NO_2 , while the coagulation of $(\text{NH}_4)_2\text{SO}_4$ with CaCO_3 exhibits an inhibiting effects at the same time. The nitrate formation is promoted in the heterogeneous

reaction of NO_2 with $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures, especially at medium RHs. ”

Page 10 line 7-9: the sentence “... therefore the heterogeneous reactions of NO_2 with the $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures were responsible for the formation of bassanite.” was revised to “... therefore the chemical interaction of $\text{Ca(NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ was responsible for the formation of bassanite in these conditions.”

Page 10 line 17-19: the sentence “And there were additional gypsum and kokaite products formed....” was revised to “Thus $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ and kokaite products could be formed both from the chemical interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca(NO}_3)_2$ and the reaction of $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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 trend of the nitrate formation rates with RH for the mixtures could be explained by the combined opposite effects from the interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca(NO}_3)_2$ 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 $\text{Ca(NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ particles may exhibit promotive effects on the nitrate formation during the heterogeneous reaction of NO_2 with $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ less than 43%. However, it was opposite for the mixtures with mass percentage of $(\text{NH}_4)_2\text{SO}_4$ larger than 57% that the nitrate formation rates and nitrate concentrations at 60% RH are smaller than those at 40% RH.”

5 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.

10 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.

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2. 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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Reply: Thanks for the reviewer's comment. The IR absorption peaks at 1008 and 1116 cm^{-1} due to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and the peaks at 1005 and 1117 cm^{-1} due to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are hard to distinguish. There are, actually, some features that can be used to differentiate $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. As has been described in this paper (page 9, line 6-9), the peaks at 1096 and 1155 cm^{-1} belong to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ can be clearly observed in the IR spectrum, which are evidences for the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ rather than $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Besides,

CaSO₄·2H₂O shows two IR-active modes in the bending modes of crystal hydrate water at 1620 and 1685 cm⁻¹, while CaSO₄·0.5H₂O 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 CaSO₄·2H₂O, at 3555 and 3610 cm⁻¹ for CaSO₄·0.5H₂O (Prasad, 2005; Liu et al., 2009).

5 ***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 CaSO₄·0.5H₂O from CaSO₄·2H₂O.”

10 ***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.

15 *Prasad, P. S. R., Krishna Chaitanya, V., Shiva Prasad, K., and Narayana Rao, D.: Direct formation of the γ -CaSO₄ 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 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.

25 ***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 HCO₃⁻ (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 HCO₃⁻, which is from the decomposition of bulk CaCO₃ 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).

5 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.

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4. 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?

Reply: Thanks for the reviewer’s advice. This sentence should be corrected to “Moreover, the surface nitrate was decreased with increasing $(\text{NH}_4)_2\text{SO}_4$ 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.

15 **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 $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ was faster than the reaction of $(\text{NH}_4)_2\text{SO}_4$ with CaCO_3 .” was misleading. What we wanted to express was that $\text{Ca}(\text{NO}_3)_2$ were more hygroscopic and soluble than CaCO_3 and it may has stronger chemical interaction with $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{Ca}(\text{NO}_3)_2$ is more hygroscopic and soluble than CaCO_3 particles.”

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6. Page 12, equation 2 and 3: Why are there two formulae for the calculation of reactive uptake coefficient? One uses $dN(\text{NO}_2)$ and the other uses $dN\text{O}_3$?

Reply: Thanks for the reviewer’s comments. In the equation 2 and 3, $N(\text{NO}_2)$ is the number of

reactive NO_2 collisions with the surface and $\{\text{NO}_3\}$ is surface concentrations of the nitrate. $d\text{N}(\text{NO}_2)/dt$ represents the rate of the reactive collisions with the surface and $d\{\text{NO}_3\}/dt$ means the nitrate formation rate. The reactive uptake coefficient (γ) 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 $(\text{NH}_4)_2\text{SO}_4\text{-CaCO}_3$ 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 (Börensén et al., 2000; Li et al., 2006; Tong et al., 2010; Ullerstam et al., 2002).

10 **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 $d\{\text{NO}_3^- \}/dt$, ...” was revised to “The rate of reactive NO_2 collision with the surface can be quantified in terms of the nitrate formation rate $d\{\text{NO}_3^- \}/dt$, ...”

References:

- 15 Börensén, 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.
- 20 Tong, S. R., Wu, L. Y., Ge, M. F., Wang, W. G., and Pu, Z. F.: Heterogeneous chemistry of monocarboxylic acids on $\alpha\text{-Al}_2\text{O}_3$ 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 Ljungström, 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.
- 25

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

Reply: Thanks for the reviewer's comments. It was reported that $\text{Ca}(\text{NO}_3)_2$ was in the state of amorphous state at $\text{RH} < 7\%$ and solution droplets at $\text{RH} > 10\%$. In this study, the $\text{Ca}(\text{NO}_3)_2$ 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 $\text{Ca}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ is responsible for the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ under dry condition and 40% RH. Figure 1a indicates that the IR absorption bands of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ are weak under dry condition (the vibration modes of water group in $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ are too weak to be identified), while the IR peaks of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ can be clearly observed at 40% RH (Figure 1b). The results indicate that the chemical interaction of $\text{Ca}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ is enhanced with the deliquescence of $\text{Ca}(\text{NO}_3)_2$. The possible reasons are that the deliquesced $\text{Ca}(\text{NO}_3)_2$ 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 $\text{Ca}(\text{NO}_3)_2$ could interact with $(\text{NH}_4)_2\text{SO}_4$ particles to form microcrystallites of NH_4NO_3 and $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$, ..." on page 14 line 3-4 was revised to "Meanwhile, the chemical interaction of $\text{Ca}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ is enhanced with the deliquescence of $\text{Ca}(\text{NO}_3)_2$, resulting in the formation of microcrystallites of NH_4NO_3 and $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$."

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.”

5 **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.”

10 **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”

15 **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.”

20 **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
25 absorb 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 SO₂ on the alkaline surface.”

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

5 **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 $\pm 1\%$ RH and $\pm 0.2^\circ\text{C}$, 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 NO₂ on CaCO₃ 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 -Al₂O₃ 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 SO₂ oxidation by O₃ 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 NO₂ did not show..." on page 9 line 25 to "In conclusion, NO₂ 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 $\text{CaCO}_3\text{-(NH}_4\text{)}_2\text{SO}_4$ 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 $N(\text{NO}_2)$ is the number of reactive NO_2 collisions with the surface, As is the effective surface area of samples and $[\text{NO}_2]$ 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 $(\text{NH}_4)_2\text{SO}_4$.” 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 $(\text{NH}_4)_2\text{SO}_4$ larger than 57%.” on page 14, line 7-9.

Heterogeneous reactions of NO₂ with CaCO₃-(NH₄)₂SO₄ mixtures at different relative humidities

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Abstract

In this work, the heterogeneous reactions of NO_2 with $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures with a series of weight percentage (wt%) of $(\text{NH}_4)_2\text{SO}_4$ were investigated using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at different relative humidity (RH) values.

5 For comparison, the heterogeneous reactions of NO_2 with pure CaCO_3 particles and pure $(\text{NH}_4)_2\text{SO}_4$ particles, as well as the reaction of CaCO_3 with $(\text{NH}_4)_2\text{SO}_4$ particles were also studied. The results indicated that NO_2 did not show any significant uptake on $(\text{NH}_4)_2\text{SO}_4$ particles, and it reacted with CaCO_3 particles to form calcium nitrate under both dry and wet conditions. The heterogeneous reactions of NO_2 with $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures were

10 markedly dependent on RH. Calcium nitrate was formed from the heterogeneous reactions at all the RHs investigated, whereas $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (bassanite), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) and $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (koktaite) were produced depending on RH. Under dry condition, the heterogeneous uptake of NO_2 on the mixtures was similar to that on CaCO_3 particles with neglectable effects from $(\text{NH}_4)_2\text{SO}_4$, the lasting time of initial stages and the NO_3^- mass

15 concentrations had negative linear relation with the mass fraction of $(\text{NH}_4)_2\text{SO}_4$ in the mixtures. Under wet conditions, the chemical interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ enhance the nitrate formation, especially at medium RHs, while the coagulation of $(\text{NH}_4)_2\text{SO}_4$ with CaCO_3 exhibits an increasing inhibiting effects with increasing RH at the same time. In

20 addition, the heterogeneous uptake of NO_2 on the mixtures of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ was found to favor the formation of bassanite and gypsum due to the decomposition of CaCO_3 and the coagulation of Ca^{2+} and SO_4^{2-} . A possible reaction mechanism was proposed and the atmospheric implications were discussed.

1. Introduction

Haze with high level of fine particulate matter with diameters less than 2.5 μm ($\text{PM}_{2.5}$) occurs frequently in China in recent years (Fang et al., 2009; Kulmala, 2015). Emissions of gaseous pollutants, e.g., SO_2 , NO_x , NH_3 , and volatile organic compounds (VOCs), result in a series of atmospheric chemical reactions, which are responsible for the formation of secondary particles and the occurrence of haze (Zhang et al., 2015; Wang et al., 2013; Guo et al., 2014). Chemical analyses show that sulfate, nitrate, and ammonium are the major aerosol constituents of $\text{PM}_{2.5}$ (Yang et al., 2011; Huang et al., 2014). Pathak et al. (2009) discovered that nitrate concentration showed a correlation with sulfate concentration as well as the RH value in ammonium-poor areas. Kong et al. (2014a) found strong negative correlation between the mass fraction of nitrate and that of sulfate in acidic atmospheric particles during air pollution episodes. Although atmospheric particulate sulfate, nitrate, and ammonium were found to be correlated by numerous field measurements in different locations (Sullivan et al., 2007; Quan et al., 2008; Duan et al., 2003; Possanzini et al., 1999; Querol et al., 1998), there is still a lack of knowledge to explain these phenomena.

Mineral dust is a major fraction of airborne particulate matter on a global scale (Tegen et al., 1996) with an estimated annual emission of 1000-3000 Tg of solids into the troposphere (Li et al., 1996). Mineral aerosols provide significant reactants and reactive sites for atmospheric heterogeneous reactions (Usher et al., 2003). Modeling studies indicated that mineral aerosols were highly associated with nitrate formation in the atmosphere (Dentener et al., 1996). Calcium carbonate represents an important and reactive mineral dust component, approximately accounting for 20-30% of the total dust loading (Usher et al., 2003; Li et al., 2006; Al-Hosney and Grassian, 2005; Prince et al., 2007). Calcium carbonate particle is converted to calcium nitrate after reaction with nitrogen oxides and HNO_3 in the atmosphere (Li et al., 2009; Laskin et al., 2005). Field measurements reveal that mineral dust particles are often mixed with ammonium sulfate aerosols through coagulation during long-range transport (Levin et al., 1996; Zhang et al., 2000). Korhonen et al. (2003) suggested that ammonium sulfate coating of mineral dust by heterogeneous nucleation of H_2SO_4 , NH_3 , and H_2O could occur at atmospheric sulphuric acid concentration. Additionally, Mori et al. (1998) have

found the coagulation between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ could form koktaite and gypsum as a result of the interaction of ions under humid condition. Ma et al. (2013) also discovered that mixed CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ particles had synergistic effects on the formation of gypsum in the humidifying-dehumidifying processes.

A few studies have shown that coexisting components play a role in the heterogeneous uptake of trace gases on atmospheric particles. Kong et al. (2014b) found that coexisting nitrate could significantly accelerate the formation rate of sulfate on hematite surface, resulting in surface-adsorbed HNO_3 , gas-phase N_2O and HONO productions. Zhao et al. (2013) found that coexisting surface nitrate had different effects on the uptake of H_2O_2 on mineral particle surfaces depending on RH. 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 (Li et al., 2007). To the best of our knowledge, the heterogeneous reaction of atmospheric trace gases on mixed CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ particles has not been reported.

Furthermore, an increase in tropospheric NO_2 concentration has been observed in recent years across many developing regions due to fossil fuel combustion and biomass burning (Zhang et al., 2007; Sheel et al., 2010; Ghude et al., 2009; Shi et al., 2008; Richter et al., 2005; Irie et al., 2005). Atmospheric NO_2 concentration ranges from 70 part per billion (ppb) during photochemical smog events to hundreds ppb in polluted urban environment (Huang et al., 2015; Zamaraev et al., 1994). NO_2 is one such critical anthropogenic gaseous pollutant, which reduces air quality and affects global tropospheric chemistry. NO_2 plays a crucial role in the photochemical induced catalytic production of ozone, leading to photochemical smog and increasing tropospheric ozone concentration (Volz and Kley, 1988). Moreover, the heterogeneous reactions of NO_2 can also lead to the deposition of nitric acid, as well as the formation of gas phase HONO (Jaegle et al., 1998; Brimblecombe and Stedman, 1982; Goodman et al., 1999). Furthermore, the heterogeneous uptake of NO_2 on mineral aerosols was responsible for the nitrate accumulation in dust events (Usher et al., 2003). A number of laboratory studies investigated the heterogeneous reaction of NO_2 with mineral dust (Underwood et al. 1999b; Bärensen et al., 2000; Finlayson-Pitts et al., 2003; Liu et al., 2015;

Guan et al., 2014). Miller and Grassian (1998) discovered that NO_2 reacted with Al_2O_3 and TiO_2 particles to form surface nitrite and nitrate. Underwood et al. (1999a) measured the uptake coefficients of NO_2 on Al_2O_3 , TiO_2 , and Fe_2O_3 particles using a Knudsen cell. Li et al. (2010) determined the Brunauer-Emmett-Teller (BET) area-corrected initial uptake coefficients to be 10^{-9} and 10^{-8} for the heterogeneous uptake of NO_2 on CaCO_3 particles under dry and wet conditions, respectively. However, there are big gaps between the results of modeling studies and field measurements about the quantities and accumulation of nitrate, especially in haze periods (Zheng et al., 2015).

In the present study, the heterogeneous reactions of NO_2 with the mixtures of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$, pure CaCO_3 particles, and pure $(\text{NH}_4)_2\text{SO}_4$ particles at different RHs were investigated using a DRIFTS reactor. The surface adsorbed products were monitored and the uptake coefficients of NO_2 were determined. The aim of this work is to explore the kinetics and mechanism of the heterogeneous reactions of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures and its relevance to RH. The results are helpful for further exploring the correlations among particulate nitrate, sulfate, and ammonium concentration in the atmosphere and partly contribute to understanding of multicomponent reaction systems in practical environment conditions.

2. Experimental

CaCO_3 (99.5 %) and $(\text{NH}_4)_2\text{SO}_4$ (99.9%) were purchased from Alfa Aesar. CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ were mechanically mixed and grinded together in order to obtain uniform mixtures with 10-93wt% (mass percent) of $(\text{NH}_4)_2\text{SO}_4$ in the mixtures, which were denoted as FAS-10, FAS-20, FAS-40, FAS-57, FAS-75, FAS-87, and FAS-93, respectively. The BET surface areas of pure CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles were determined to be 8.15 and 0.19 $\text{m}^2 \text{g}^{-1}$, respectively, (Autosorb-1-MP automatic equipment (Quanta Chrome Instrument Co.)). The BET area of the mixtures were determined to be 8.06, 6.62, 4.54, 3.21, 2.34, 1.67, and 0.89 $\text{m}^2 \text{g}^{-1}$ corresponding to the mixtures mentioned above. NO_2 (0.1%, Beijing Huayuan Gas Chemical Industry Co., Ltd.) and N_2 (>99.999%, Beijing Tailong Electronics Co., Ltd.) were used in this study.

In the gas supply system, N₂ was split into two streams; one was dehumidified by silica gel and molecular sieve to insure RH less than 1% which was called dry condition, the other one was humidified by bubbling through ultrapure water. The flux of dry N₂, humid N₂, and NO₂ were adjusted to reach desired RH (<1%, 40%, 60%, and 85% RH) conditions with the total
5 flow of 400 sccm by using mass flow controllers (Beijing Sevenstar electronics Co., LTD). Concentration of NO₂ entering reactor was diluted to 2.6×10^{15} molecules cm⁻³ by mixing with N₂. RH and temperature of the inflow of sample cell were measured using a commercial humidity and temperature sensor (HMT330; Vaisala) with a measurement accuracy of $\pm 1\%$ RH and $\pm 0.2^\circ\text{C}$, respectively.

10 In situ DRIFTS experiment was used to monitor reactions in real time without interrupting the reaction processes and provide mechanistic details and kinetic data (Vogt and Finlaysonpitts, 1994). Infrared spectra of sample surfaces were recorded with a Nicolet FTIR Spectrometer 6700, which was equipped with a liquid-nitrogen-cooled narrow band mercury-cadmium-telluride (MCT) detector and DRIFTS optics (Model CHC-CHA-3,
15 Harrick Scientific Corp.). The DRIFTS equipment has been described elsewhere (Tong et al., 2010). The spectra were measured at a resolution of 4 cm⁻¹ in the spectral range from 4000 to 650 cm⁻¹. Each spectrum was generally averaged from 100 scans with a time resolution of 40 s. In situ DRIFTS experiments were carried out on CaCO₃-(NH₄)₂SO₄ mixtures, CaCO₃ particles, and (NH₄)₂SO₄ particles, respectively. About 30 mg samples were placed into the
20 stainless steel sample holder (10 mm diameter, 0.5 mm depth). The investigated samples were exposed to pure nitrogen with desired RH for 20 minutes to establish adsorption equilibrium. Then infrared spectra of the unreacted powder samples were collected as background so that reaction products were observed as positive adsorption bands while losses of surface species as negative adsorption bands. Subsequently, NO₂ was introduced into the reaction chamber at
25 a stable RH for 120 min. All the spectra were automatically collected through a Series program in OMNIC software.

The products formed on the samples after reaction with NO₂ were analyzed by ion chromatography. The filtered solution was analyzed by using a Dionex ICS 900system, equipped with a Dionex AS 14A analytical column and a conductivity detector (DS5). The

reacted samples were sonicated for 20 min in 8 ml ultrapure water.

3. Results and discussion

3.1 Surface products characterization

5 Figure 1 represents the IR spectra of surface products when the samples were exposed to NO_2 for 120 min at different RHs. Under dry condition (Fig. 1a), absorption bands centered at 746, 816, 1040, 1300, and 1330 cm^{-1} which were assigned to surface nitrate could be observed on CaCO_3 particle surfaces (FAS-0) and the mixtures (Goodman et al., 2001; Goodman et al., 2000; Al-Hosney and Grassian, 2005). Moreover, peaks at 1630 and 3540 cm^{-1} were assigned
10 to crystal hydrate water in calcium nitrate (Li et al., 2010). It suggested that calcium nitrate was formed on CaCO_3 particle surfaces and the mixtures of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$. The detailed vibrational assignments were listed in Table 1. Two peaks observed at 1689 and 838 cm^{-1} could be attributed to the $\nu(\text{C}=\text{O})$ and $\delta_{\text{oop}}(\text{CO}_3)$ of adsorbed carbonic acid, respectively, indicating that carbonic acid acted as an intermediate production under dry condition
15 (Al-Hosney and Grassian, 2004; Al-Abadleh et al., 2004). Besides, adsorbed nitric acid was also formed with peaks centered at 1710 and 1670 cm^{-1} , which were assigned to the asymmetric stretching of adsorbed nitric acid (Goodman et al., 1999). At the same time, negative bands ranging from 2800 to 3400 cm^{-1} could be ascribed to the loss of surface adsorbed water and negative peaks at 3640 and 3690 cm^{-1} were corresponding to the two
20 types of hydroxyl ions on CaCO_3 particle surfaces (Kuriyavar et al., 2000). No obvious negative peaks could be observed when the samples exposed to dry pure nitrogen for 120 min which indicated that surface adsorbed water and hydroxyl ions participated in the reaction.

Compared with the spectrum of FAS-0, several additional weak absorptions appeared at 1008, 1096, 1155 cm^{-1} on the CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures, which could be attributed to the
25 vibration modes of SO_4 tetrahedra in $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (bassanite) (Prasad, 2005; Liu et al., 2009). The vibration modes of water group in bassanite were too weak to be observed. In addition, the peak at 1215 cm^{-1} slightly grew in intensity during the whole heterogeneous reaction period of NO_2 with the mixtures, whereas it grew fast at the early stage of the

reaction of NO_2 with CaCO_3 particles, and then diminished after reaching a maximum value at about 30 min (see Fig. S1). This band described before was ascribed to nitrite species, which would convert to nitrate as the reaction proceeded (Miller and Grassian, 1998; G. M. Underwood, 1999b; Wu et al., 2013). To probe this product, samples after reaction with NO_2 for different times were detected by IC. The results showed that nitrite was increased during the first 30 min in the reaction of NO_2 with CaCO_3 particles, whereas it was too little to be detected after the reaction lasted about 60 min.

At 40% RH (Fig. 1b), the absorption bands of nitrate shifted from 1040 cm^{-1} to 1043 cm^{-1} , 746 cm^{-1} to 749 cm^{-1} , and 816 cm^{-1} to 828 cm^{-1} , respectively, compared to those under dry condition. Meanwhile, the shoulder peak at 1300 cm^{-1} belong to asymmetric stretching of nitrate became ambiguous. The frequency shifts of nitrate adsorption bands were caused by the phase transition of calcium nitrate. It was reported that calcium nitrate was in amorphous hydrates state at RH below 7% (Liu et al., 2008), and it deliquesced to form a saturated solution droplet at 18% RH (Tang and Fung, 1997). For the absorption bands of nitrate on the mixtures of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$, there was a new shoulder peak at 1365 cm^{-1} which were attributed to the $\nu_3(\text{NO}_3)$ in NH_4NO_3 (Schlenker et al., 2004). Moreover, the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ was enhanced at 40% RH compared to that under dry condition, as features became apparent at 1155, 1096, and 1008 cm^{-1} , concomitant with the appearance of the peaks at 1620, 3555, and 3605 cm^{-1} due to the vibration modes of water group in bassanite (Prasad et al., 2005). Additionally, signatures at 1670 cm^{-1} , 1570 cm^{-1} on the samples suggested the formation of nitric acid and HCO_3^- during the heterogeneous reaction, respectively. And the signature at 1189 cm^{-1} (Schlenker et al., 2004) on the mixtures suggested that HSO_4^- was produced.

When RH reached 60% (Fig. 1c), water film was formed on particle surfaces with a band centered at 1650 cm^{-1} and a broad band composed of three peaks at 3260, 3400, and 3570 cm^{-1} , which could be assigned to the vibration modes of surface condensed water (Al-Abadleh et al., 2000). Meanwhile, the asymmetric stretching of surface nitrate appeared as a sharp peak at 1338 cm^{-1} . This was likely due to calcium nitrate incorporated into surface adsorbed water film and formed free aquated ions, based on the truth that only one sharp asymmetric

stretching peak existed for free aquated ions NO_3^- (Gatehouse et al., 1957). The absorptions bands due to NH_4NO_3 could also be observed at 1365 cm^{-1} for the mixtures of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$. Additionally, new peaks could be observed at 1168, 1145, and 1117 cm^{-1} , which were attributed to the $\nu_3(\text{SO}_4)$ mode of gypsum. 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 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Gypsum showed two IR-active modes in the bending modes of crystal hydrate water at 1620 and 1685 cm^{-1} , while bassanite had only one band at 1620 cm^{-1} . And the two stretching modes of crystal hydrate water appeared at 3545 , and 3400 cm^{-1} for gypsum, at 3555 and 3610 cm^{-1} for bassanite (Prasad, 2005). Furthermore, it should be noticed that the peak at 3400 cm^{-1} from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on the samples of FAS-40, FAS-57, FAS-75, and FAS-87 were much stronger than the peak at 3400 cm^{-1} from condensed water on CaCO_3 particles. Therefore it can be inferred that $\text{Ca}(\text{NO}_3)_2$, NH_4NO_3 , $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ (gypsum and bassanite) were produced at 60% RH from the heterogeneous reaction of NO_2 with the CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures.

The spectrum of FAS-0 in Fig. 1d was similar to that in Fig. 1c, while there were considerable changes for spectra of the mixtures as RH increased to 85%. Peaks observed at 981, 998, 1131, 1177 cm^{-1} on the mixtures due to the stretching vibration modes of SO_4^{2-} as well as peaks at 2860, 3064, 3192 cm^{-1} assigned to the stretching vibration modes of NH_4^+ indicated the formation of $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (koktaite) (Jentzsch et al., 2012). The absorption band of nitrate overlapped with that of koktaite at 749 cm^{-1} . It can be inferred that koktaite, an intermediate production of gypsum, was formed rapidly as a result of the interaction of ions in the liquid film after the deliquescence of $(\text{NH}_4)_2\text{SO}_4$ and surface salts (Cziczo et al., 1997; Lightstone et al., 2000). Additionally, the IR absorption peaks at 1570 cm^{-1} in Figure 1d are much stronger than those at 40% and 60% RH. The positive intensity is likely due to the increasing information of HCO_3^- , which is from the decomposition of the bulk CaCO_3 under wet conditions. It can 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 is enhanced as a result of the

formation of HNO_3 and the dissolution of $(\text{NH}_4)_2\text{SO}_4$, which facilitates the decomposition of bulk CaCO_3 .

In conclusion, NO_2 did not show any significant uptake on pure $(\text{NH}_4)_2\text{SO}_4$ particles (FAS-100) at all the RHs investigated. And the products formed from the heterogeneous reactions of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures were strongly dependent on RH. $\text{Ca}(\text{NO}_3)_2$ was produced under both dry and wet conditions, bassanite, gypsum and koktaite were formed depending on RH.

In another set of experiments, the mixture of FAS-57 was exposed to nitrogen without the introduction of NO_2 in order to investigate the solid-state reaction of CaCO_3 with $(\text{NH}_4)_2\text{SO}_4$.

As shown in Fig. 2, no new absorption bands occurred after exposing to dry nitrogen for 120 min. The weak peak at 1189 cm^{-1} due to HSO_4^- appeared as a main absorption peak and no obvious absorption band due to $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ could be observed at 40% RH. The results suggested that little reaction occurred between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles under dry condition and 40% RH. Therefore the chemical interaction of $\text{Ca}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ was

responsible for the formation of bassanite in these conditions. This is likely due to the fact that $\text{Ca}(\text{NO}_3)_2$ is more hygroscopic and soluble than CaCO_3 particles. Furthermore, absorption bands

attributed to bassanite, gypsum, koktaite, and surface water film could be observed at 60% and 85% RH, indicating that a chemical reaction in the coagulation of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles actually occurred at 60% and 85% RH without the introduction of NO_2 . This result

was in good agreement with the results reported by Mori et al. (1998) that gypsum was formed from the chemical reaction between $(\text{NH}_4)_2\text{SO}_4$ and CaCO_3 with koktaite acting as an intermediate product at 70% RH. In addition, the integrated absorbance of bands between 1100 and 1250 cm^{-1} for the sample of FAS-57 at 60% and 85% RH in Fig. 2 were about fifty percent and seventy percent of those for FAS-57 at corresponding RH in Fig. 1. Thus

$\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ and koktaite products could be formed both from the chemical interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ and the reaction of $(\text{NH}_4)_2\text{SO}_4$ with CaCO_3 at 60% and 85% RH.

3.2 Uptake coefficients and kinetics

The formation rates of nitrate on CaCO_3 particle surfaces and the mixtures were studied. The nitrate formed during the reaction was presented by the integrated absorbance (I_A) of the IR peak area between 1390 and 1250 cm^{-1} . The peak at 1043 cm^{-1} was not used to avoid the interruption of the absorptions of sulfates. The integrated nitrate absorbance over the ν_1 region (1013-1073 cm^{-1}) and the ν_3 region (1250-1390 cm^{-1}) could well overlap after the former multiplied by a constant on CaCO_3 particle surfaces (Figure S2). Figure 3 represents the integrated absorbance of nitrate as a function of time at different RHs. 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 slowed down at stable stage after a transition period. Furthermore, the lasting time of initial stages for the mixtures decreased nearly linearly with increasing mass fraction of $(\text{NH}_4)_2\text{SO}_4$ in the mixtures, e.g., it lasted about 80 min for FAS-0 (pure CaCO_3 particles), 30 min for FAS-57, 20 min for FAS-75 and 5 min for FAS-93. In another word, the reactive ability of the mixtures in initial stage had a positive linear relation with the CaCO_3 content in the mixtures.

The possible reasons were that for the reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures, nitrate was formed by the uptake of NO_2 on CaCO_3 particle surfaces without the participation of $(\text{NH}_4)_2\text{SO}_4$ and the reactions limited on the surfaces under dry condition. Moreover, the lasting time of initial stages were extended with increasing RH, e.g., it extended to 80 min for the mixture of FAS-75, to 50 min for the mixture of FAS-93, and even may longer than 120 min for the mixtures with mass fraction of $(\text{NH}_4)_2\text{SO}_4$ smaller than 57% at 40% RH. The boundaries between initial stages and transition stages became ambiguous at 60% RH and finally disappeared at 85% RH for all the CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures. This was likely due to the fact that the reaction of NO_2 could react into the bulk of the particles under wet conditions.

The integrated absorbance (I_A) for nitrate ions on the samples had a linear relationship with the amount of nitrate determined by ion chromatography $\{\text{NO}_3^-\}$:

$$\text{The nitrate ions: } \{\text{NO}_3^-\} = (\text{integrated absorbance } I_A) \times f \quad (1)$$

Here f is conversion factor. It is calculated to be $(2.14 \pm 0.17) \times 10^{17}$ ions/int.abs at 85% RH

and $(3.32 \pm 0.13) \times 10^{17}$ ions/int.abs at 60% RH, 40% RH and dry condition (see Fig. S3). The conversion factor f may change with the chemical environment of surface nitrate which is related to surface condensed water and ion interaction (Li et al., 2010). Then nitrate formation rates $d\{\text{NO}_3^-\}/dt$ can be calculated from f and the slope of integrated absorbance as a function of time.

As shown in Fig. 4, the initial nitrate formation rates for the samples showed a maximum value under dry condition, whereas the stable formation rates were much slower in this condition. The initial nitrate formation rates increased slightly as RH increased from 40% RH to 60% and 85% RH for the uptake of NO_2 on CaCO_3 particle surfaces (FAS-0). For the mixtures with mass fraction of $(\text{NH}_4)_2\text{SO}_4$ larger than 57%, it showed an opposite variation that initial nitrate formation rates at 40% RH were higher than that at 60% RH, followed by that at 85% RH. While for the mixtures with mass fraction of $(\text{NH}_4)_2\text{SO}_4$ 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 tendency of nitrate formation rates with RH for the mixtures could be explained by the combined opposite effects from the interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ or CaCO_3 at 60% RH.

Besides, nitrate formation rates decreased more evidently with increasing $(\text{NH}_4)_2\text{SO}_4$ content at 85% RH and dry condition than at 40% and 60% RH, e.g., the initial nitrate formation rates for the mixture of FAS-93 under dry condition, 40%, 60%, and 85% RH were 47%, 70%, 62%, and 34% of that for FAS-0 at corresponding RH, respectively. Furthermore 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, e.g., the initial nitrate formation rates for FAS-0 at 40%, 60%, and 85% RH were 64%, 67%, and 72% of that under dry condition, respectively, for the mixture of FAS-93, the initial nitrate formation rates at 40%, 60%, and 85% RH were 95%, 87%, and 60% of that under dry condition. In conclusion, the initial nitrate formation rates were accelerated to an extent at 40% and 60% RH, whereas it was inhibited slightly at 85% RH.

The reactive uptake coefficient (γ) is defined as the rate of the reactive collisions with the surface divided by the total number of surface collisions per unit time (Z).

$$\gamma = \frac{dN(\text{NO}_2)/dt}{Z} \quad (2)$$

$$Z = \frac{1}{4} A_{\text{surface}} [\text{NO}_2] \sqrt{\frac{8RT}{\pi M_{\text{NO}_2}}} \quad (3)$$

5 Where $N(\text{NO}_2)$ is the number of reactive NO_2 collisions with the surface, A_{surface} is the effective surface area of samples and $[\text{NO}_2]$ is the gas-phase concentration of NO_2 . R represents the gas constant, T represents the temperature and M_{NO_2} is the molecular weight of NO_2 . The rate of reactive NO_2 collision with the surface can be quantified in terms of the nitrate formation rate $d\{\text{NO}_3^-\}/dt$, then the reactive uptake coefficients can be calculated by:

$$\gamma = \frac{d\{\text{NO}_3^-\}/dt}{Z} \quad (4)$$

The uptake coefficients of NO_2 on CaCO_3 particles and $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures were calculated using both BET and geometric surface area, which could be considered as two extreme cases (Ullerstam et al., 2002). The results are listed in Table 2. The initial uptake coefficients corresponding to BET surface area for NO_2 on CaCO_3 particle surfaces are
 15 $(3.34 \pm 0.14) \times 10^{-9}$, $(2.04 \pm 0.07) \times 10^{-9}$, $(2.23 \pm 0.22) \times 10^{-9}$, and $(2.28 \pm 0.17) \times 10^{-9}$ for dry condition, 40%, 60%, and 85% RH, respectively, well consistent with the previous measurement results (Li et al., 2010; B rensen et al., 2000). The γ_{BET} is approximately a factor of 10^4 smaller than the $\gamma_{\text{geometric}}$. The γ_{BET} for the uptake of NO_2 on the mixtures was enhanced with increasing $(\text{NH}_4)_2\text{SO}_4$ content because of the decrease of BET surface area. On the contrary, the $\gamma_{\text{geometric}}$
 20 decreased with increasing $(\text{NH}_4)_2\text{SO}_4$ content due to the decrease of nitrate formation rates.

The mass concentrations of NO_3^- formed on the samples after reaction with NO_2 were detected by IC, as shown in Fig. 5. The NO_3^- mass concentrations for CaCO_3 particles are 3.22 ± 0.17 , 3.31 ± 0.03 , 3.38 ± 0.35 , and 3.47 ± 0.32 mg/g under dry condition, 40%, 60% and 85% RH, respectively. It suggests that the NO_3^- mass concentration increase slightly with higher
 25 RH for the reaction of NO_2 with CaCO_3 particles. For the $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures, the

NO_3^- mass concentrations under dry condition are obviously smaller than those at 85% RH, and it exhibits maximum values at 40% or 60% RH. In addition, it should be noticed that the NO_3^- mass concentrations has a negative linear relation with $(\text{NH}_4)_2\text{SO}_4$ mass fraction in the mixtures under dry condition, the R^2 of liner fit is 0.993. This result is in good agreement with the conclusions of Figure 1a and Figure 3 that the reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures is very similar to the reaction of NO_2 with pure CaCO_3 particles under dry condition and that $(\text{NH}_4)_2\text{SO}_4$ has little effects on the formation of NO_3^- in this condition. Moreover, the concentrations of NO_3^- of the mixtures under wet conditions are markedly larger than those under dry condition. The nitrate concentrations for the mixtures of FAS-10 and FAS-20 at 40% and 60% RH are even larger than that for pure CaCO_3 particles. 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., the NO_3^- mass concentrations for the mixture of FAS-57 are 3.23 ± 0.09 , 3.09 ± 0.14 , 2.42 ± 0.07 mg/g at 40%, 60% and 85% RH, respectively, which are increased by a factor of 2.1, 2.0, and 1.6 in comparison with that for FAS-57 under dry condition (1.55 ± 0.08 mg/g). For the reaction of NO_2 with FAS-0, the NO_3^- mass concentrations just increase by a factor of 1.03, 1.05, 1.08, as RH increased from dry condition to 40%, 60% and 85% RH, respectively. Besides, no obvious NO_3^- is formed on pure $(\text{NH}_4)_2\text{SO}_4$ particles under all conditions investigated. These results clearly reveal that the CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures exhibit promotive effects on nitrate formation in the heterogeneous reaction with NO_2 under wet conditions.

The results described above indicate that relative humidity plays a vital role in the heterogeneous reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures. Under dry condition, little reaction occurs between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$. Therefore, nitrate formed on the mixtures under dry condition is mainly produced from the reaction of NO_2 with CaCO_3 particles. At 40% RH, the solid-state reaction between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles can be neglected, implying that the solid-state reaction has little effects on the heterogeneous reaction. Meanwhile, the chemical interaction of $\text{Ca}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{SO}_4$ is enhanced with the deliquescence of $\text{Ca}(\text{NO}_3)_2$, resulting in the formation of microcrystallites of NH_4NO_3 and $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$. Consequently, it may help to improve 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). Thus the chemical interaction of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ particles may exhibits promotive effects on the nitrate formation during the heterogeneous reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures. 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 $(\text{NH}_4)_2\text{SO}_4$ less than 43%. However, it was opposite for the mixtures with mass percentage of $(\text{NH}_4)_2\text{SO}_4$ larger than 57%. This could be possibly explained that there is a

combined effect of the two opposing effects on nitrate formation from the interaction of $(\text{NH}_4)_2\text{SO}_4$ with $\text{Ca}(\text{NO}_3)_2$ or CaCO_3 during the heterogeneous reaction of the mixtures with NO_2 . Since a chemical reaction in the coagulation of CaCO_3 with $(\text{NH}_4)_2\text{SO}_4$ actually

occurred without the introduction of NO_2 at 60% RH, leading to the formation of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$. Consequently, CaCO_3 particles are partly consumed during the coagulation process and $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ formed in the coagulation may block reactive sites for further reaction. Thus, the solid state reaction between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles exhibits inhibiting effects on the formation of nitrate on the mixtures. As for 85% RH, the deliquescence of $(\text{NH}_4)_2\text{SO}_4$ and surface nitrate leads to more water uptake on the mixture surfaces. The inhibiting effects from the coagulation of CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ in water film become stronger at 85% RH than at 60% RH, resulting in the decrease of nitrate formation rates and nitrate concentrations at 85% RH in comparison with those at 40% and 60% RH.

3.3 Mechanism

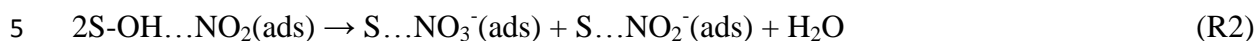
According to the experimental observations described above, a reaction mechanism for the heterogeneous reactions of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures was proposed.

Gas phase NO_2 attached to surface OH groups on CaCO_3 particle surfaces, as shown in (R1), where (g) is the gas phase and (ads) is the adsorbed phase.

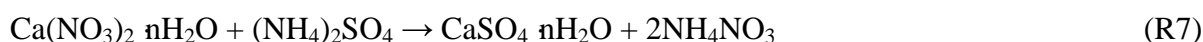


Börensén et al. (2000) proposed that two adsorbed-phase NO_2 molecules result in surface

nitrate and nitrite products through a disproportionation reaction. Underwood et al. (1999b) suggested that NO₂ (g) reacted to form adsorbed nitrite species initially and then react with another surface nitrite or with gas-phase NO₂ to form nitrate. Nitrite was detected by FTIR and IC in this study. The reaction process can be described as:



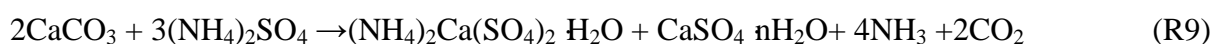
Under dry condition, the surface nitrate was in equilibrium with surface adsorbed water and adsorbed HNO₃ species (R5). Adsorbed H₂CO₃ can exist on CaCO₃ particle surfaces (R6) and
10 there was weak chemical interaction between Ca(NO₃)₂ and (NH₄)₂SO₄ (R7).



At 40% RH, Ca(NO₃)₂ deliquesced to form a solution droplet and reacted with (NH₄)₂SO₄:



At 60% RH, the interaction between CaCO₃ and (NH₄)₂SO₄ in the presence of surface adsorbed water film can be expressed as R9:



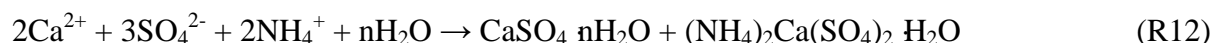
It should be noticed that NH₃ was detected by PTR-MS (Proton-transfer-reaction mass
20 spectrometry) under wet conditions in this study. NH₃ can also be released from the decomposition of NH₄NO₃ (R10).



At the same time, the heterogeneous reaction of NO₂ with surface adsorbed water has been demonstrated to form adsorbed HNO₃(ads) and gaseous HONO(g) (Svensson et al., 1987;
25 Jenkin et al., 1988; Goodman et al., 1999).



At 85% RH, the interaction of ions in the water film can be expressed as:



5 4. Conclusions and atmospheric implications

The surface products and kinetics of the heterogeneous reactions of NO_2 with CaCO_3 particles, $(\text{NH}_4)_2\text{SO}_4$ particles, and CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures were investigated under various RHs, using DRIFTS technique. And the solid-state reaction between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles were studied for comparison. All these reactions can occur in practical atmospheric conditions, which can be expressed in Fig. 6. The findings in this study have important atmospheric implications.

Calcium nitrate was produced from the heterogeneous reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures under both dry and wet conditions, and bassanite, gypsum and koktaite were formed depending on RH. It suggested that chemical composition in particulate phase was changed during the heterogeneous process, which can affect the physicochemical characteristics of atmospheric particles, including hygroscopicity, optical properties, and chemical reactivity. Besides, koktaite was detected in aerosols collected in Beijing, while it was absent in the soil where the dust originates (Mori et al., 2003), large uncertainties remain about its formation in the atmosphere. The results presented here provide evidence that the heterogeneous reactions of mixed CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ particles with atmospheric acid trace gases was a possible source of koktaite. Also, the results indicated that the uptake of NO_2 and the formation of nitrate promoted removing SO_4^{2-} from water soluble species to insoluble gypsum species, which could reduce the atmospheric water soluble sulfate content.

Gas phase products such as NH_3 could be released during the heterogeneous reaction of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures. In the atmosphere NH_3 is mainly emitted from agriculture activities (such as fertilization and animal feeding) and biomass burning, and it plays an important role in nucleation and the growth of ion cluster and nanoparticles. The

results in this study suggest that heterogeneous uptake of NO_2 on CaCO_3 particles with the presence of $(\text{NH}_4)_2\text{SO}_4$ may be a potential pathway for the transformation of NH_3 from particulate phase to gas phase.

Furthermore, the uptake-coefficients of NO_2 on CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures were determined, providing kinetic data for modeling studies. The results illustrate that the presence of $(\text{NH}_4)_2\text{SO}_4$ exhibits a promotive effect on the nitrate formation under wet conditions as a result of the interaction between $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$. On the contrary, the reaction between CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles has an inhibiting effect on the formation of nitrate during the heterogeneous reaction process, especially at high RH. Considering the abundance of $(\text{NH}_4)_2\text{SO}_4$ in the atmospheric aerosols, its mixtures with mineral dust may affect nitrate formation and the content of nitrate in atmospheric particles. The multicomponent reaction systems under ambient RH conditions play potentially vital role in atmospheric processes. To better understand the role of heterogeneous reactions in the atmospheric chemistry, the effects of ambient RH as well as multicomponent reaction systems should be considered.

The Supplement related to this article is available online.

Author contributions. Fang Tan and Shengrui Tong contribute equally to this work.

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Table 1. Assignments of IR vibration frequencies of surface adsorbed species formed on CaCO_3 particle surfaces and $\text{CaCO}_3\text{-(NH}_4)_2\text{SO}_4$ mixtures

Samples	Stretch mode	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	Stretch mode	
$\text{Ca(NO}_3)_2$	NO_3^-	1043	816	1300, 1330,	748		
$^a\text{NH}_4\text{NO}_3$	NO_3^-	1050	830	1333, 1365		NH_4^+	1426, 1451
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	SO_4^{2-}	1008		1096, 1116, 1155, 1168		H_2O	1620, 3553, 3605
$^b\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	SO_4^{2-}	1008		1096, 1116, 1153, 1168	601, 660	H_2O	1620, 3550, 3610
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	SO_4^{2-}	1003		1117, 1145, 1167		H_2O	1620, 1685, 3400, 3545
$^c\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	SO_4^{2-}	1005		1117, 1145, 1167	602, 669	H_2O	1621, 1685, 3405, 3495, 3547
$(\text{NH}_4)_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$	SO_4^{2-}	981, 998		1131, 1177		H_2O	2860, 3064, 3192
$^d(\text{NH}_4)_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$	SO_4^{2-}	981, 998		1108, 1131, 1177	602, 614, 646, 656	H_2O	2857, 2922, 3125, 3192

^a from Schlenker et al. (2004). ^{b,c} from Prasad et al. (2005). ^d from Jentzsch et al. (2012)

Table 2. Initial uptake coefficients calculated using BET surface area and geometric surface area for the reaction of NO₂ with CaCO₃ particle surfaces and CaCO₃-(NH₄)₂SO₄ mixtures at various RHs.

(NH ₄) ₂ SO ₄ (wt%)	dry condition		40% RH		60% RH		85% RH	
	γ_{BET} ($\times 10^{-9}$)	γ_{geo} ($\times 10^{-6}$)	γ_{BET} ($\times 10^{-9}$)	γ_{geo} ($\times 10^{-6}$)	γ_{BET} ($\times 10^{-9}$)	γ_{geo} ($\times 10^{-6}$)	γ_{BET} ($\times 10^{-9}$)	γ_{geo} ($\times 10^{-6}$)
0	3.34 \pm 0.14	10.4 \pm 0.44	2.04 \pm 0.07	6.36 \pm 0.22	2.23 \pm 0.22	6.94 \pm 0.69	2.28 \pm 0.17	7.10 \pm 0.53
10	3.19 \pm 0.21	9.83 \pm 0.65	2.06 \pm 0.21	6.34 \pm 0.45	2.25 \pm 0.14	6.91 \pm 0.43	2.13 \pm 0.41	6.56 \pm 1.26
20	3.77 \pm 0.24	9.54 \pm 0.61	2.51 \pm 0.34	6.28 \pm 0.86	2.74 \pm 0.42	6.87 \pm 1.06	2.00 \pm 0.21	5.63 \pm 0.53
40	5.34 \pm 0.17	9.25 \pm 0.29	3.50 \pm 0.42	6.07 \pm 0.72	3.67 \pm 0.48	6.36 \pm 0.83	3.15 \pm 0.28	5.46 \pm 0.49
57	6.82 \pm 0.33	8.38 \pm 0.41	4.70 \pm 0.51	5.78 \pm 0.63	4.47 \pm 0.26	5.49 \pm 0.32	4.15 \pm 0.53	5.10 \pm 0.65
75	7.74 \pm 0.94	6.94 \pm 0.84	6.12 \pm 0.37	5.49 \pm 0.23	5.80 \pm 0.53	5.20 \pm 0.48	4.26 \pm 0.31	3.82 \pm 0.28
87	9.04 \pm 0.73	5.78 \pm 0.46	7.68 \pm 0.50	4.92 \pm 0.32	7.22 \pm 0.63	4.63 \pm 0.40	4.83 \pm 0.46	3.10 \pm 0.19
93	14.4 \pm 1.07	4.90 \pm 0.36	13.6 \pm 0.93	4.63 \pm 0.32	12.7 \pm 0.81	4.34 \pm 0.28	7.48 \pm 0.82	2.55 \pm 0.28

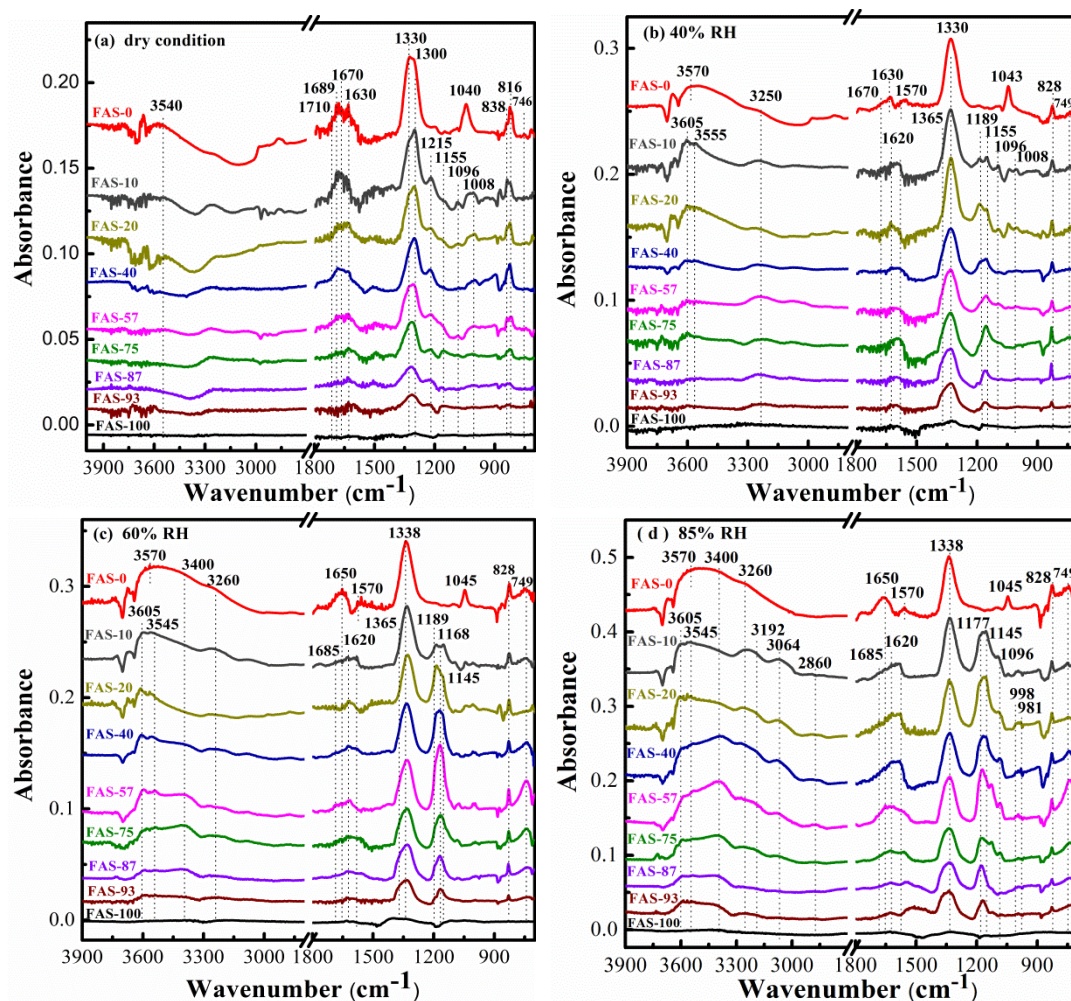


Figure 1. DRIFTS spectra of CaCO_3 particles (FAS-0), CaCO_3 -(NH_4) $_2\text{SO}_4$ mixtures (FAS-10 - FAS-93), and (NH_4) $_2\text{SO}_4$ particles (FAS-100) after reaction with NO_2 at (a) dry condition, (b) 40% RH, (c) 60% RH, (d) 85% RH for 120 min. The concentration of NO_2 was 2.6×10^{15} molecule cm^{-3} .

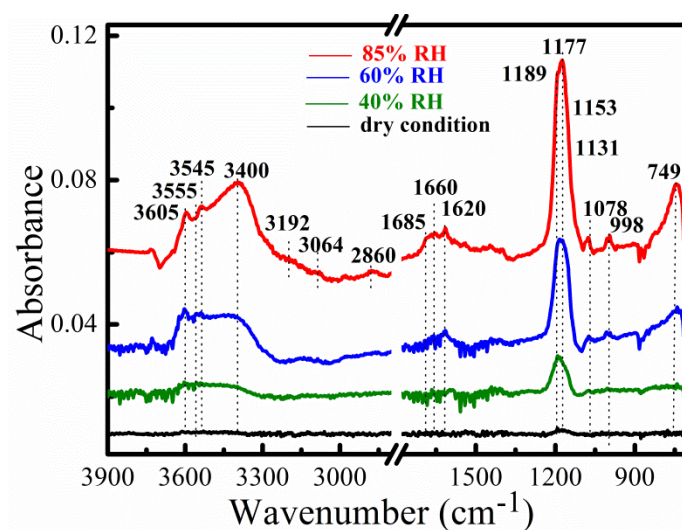


Figure 2. In situ DRIFTS spectra of surface products when the mixture of FAS-57 were exposed to nitrogen at dry condition (black), 40% RH (green), 60% RH (blue) and 85% RH (red) for 120 min.

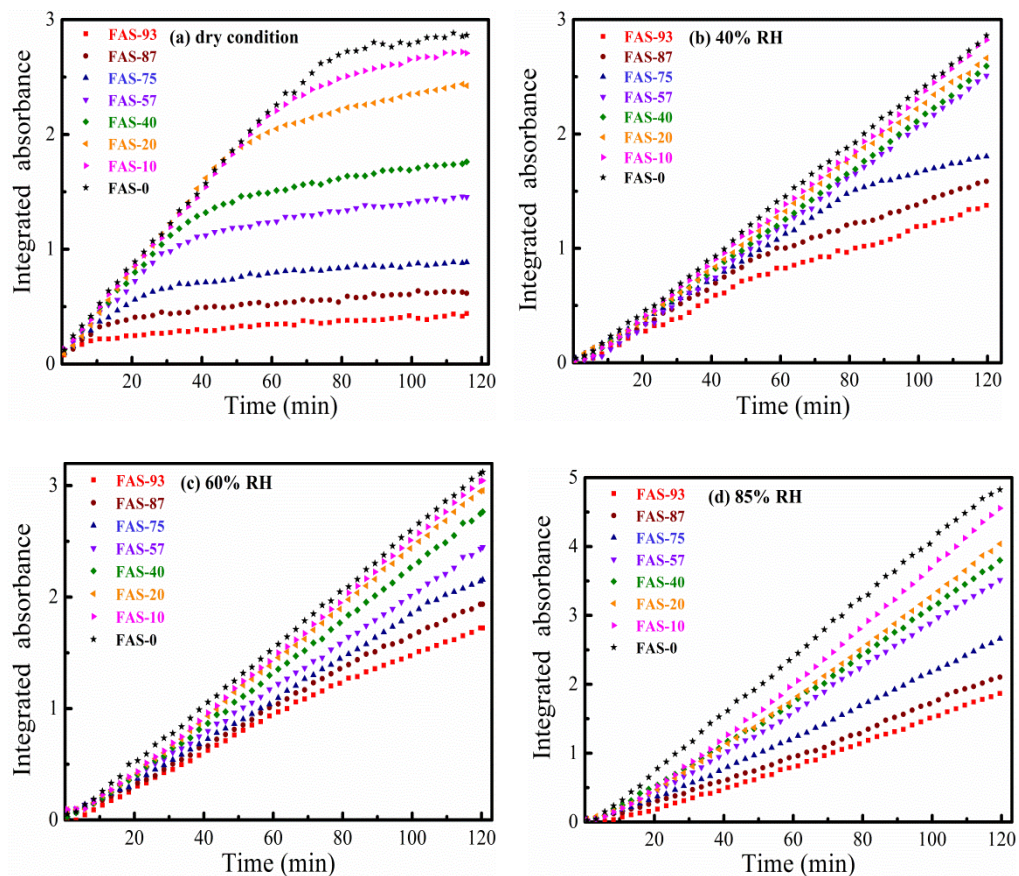


Figure 3. The integrated absorbance of the peak area between 1390 and 1250 cm^{-1} for nitrate on pure CaCO_3 particle surfaces (FAS-0), and $\text{CaCO}_3\text{-(NH}_4\text{)}_2\text{SO}_4$ mixtures (FAS-10 - FAS-93) at (a) dry condition, (b) 40% RH, (c) 60% RH, and (d) 85% RH. The NO_2 concentration was $2.6 \times 10^{15} \text{ molecule cm}^{-3}$.

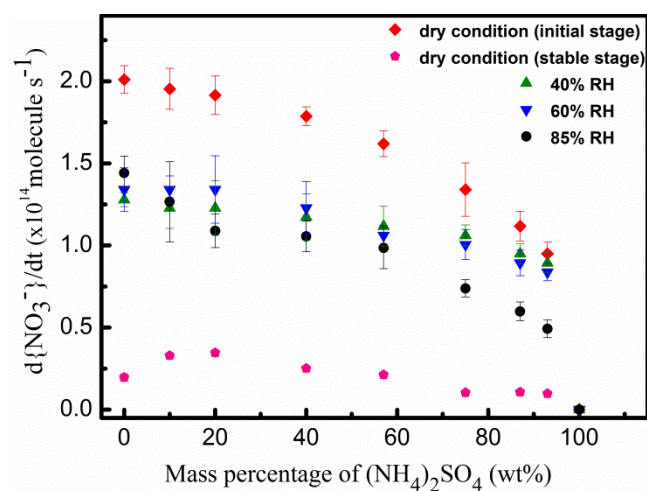


Figure 4. Initial nitrate formation rates at dry condition (rhombus), 40% RH (triangle), 60% RH (fall triangle), 85% RH (roundness) and stable nitrate formation rates (pentagon) under dry condition versus the mass percentage of $(NH_4)_2SO_4$ in the mixtures. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.

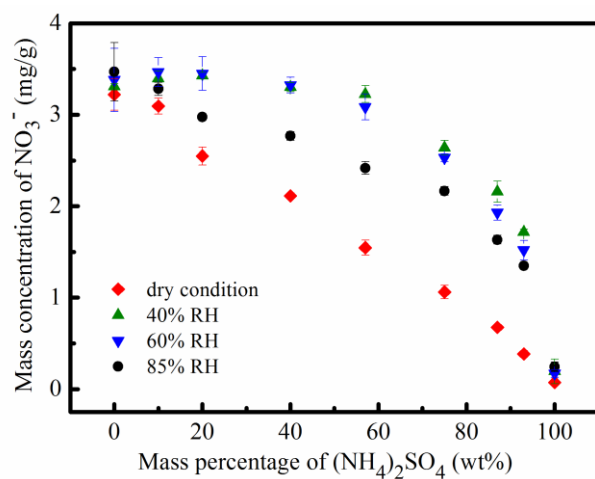


Figure 5. The mass concentration of NO₃⁻ for CaCO₃ particles and the CaCO₃-(NH₄)₂SO₄ mixtures after reacted with NO₂ for 120 min as a function of the mass percentage of (NH₄)₂SO₄ in the mixtures. The data points and the error bars are the average value and the standard deviation of three duplicate experiments.

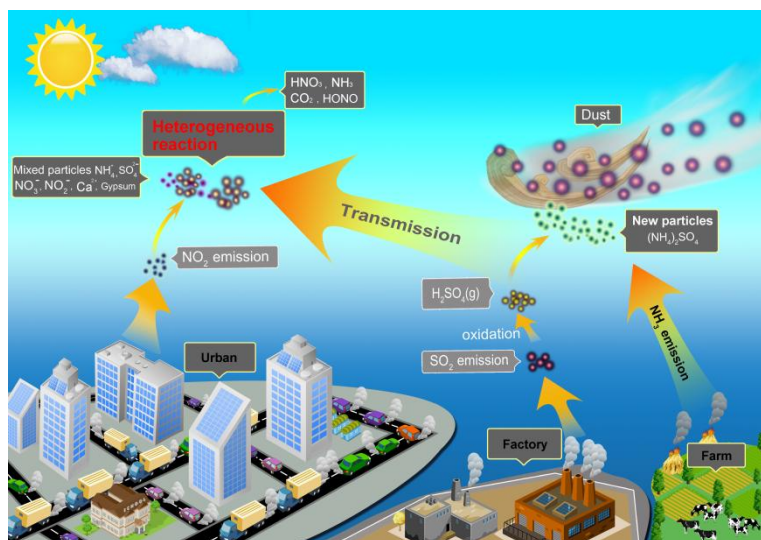


Figure 6. Schematic illustrating the possible heterogeneous processes of NO_2 with CaCO_3 - $(\text{NH}_4)_2\text{SO}_4$ mixtures and the possible atmospheric implications.