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Comment

## ***Interactive comment on “Kinetics and mechanisms of heterogeneous reaction of NO<sub>2</sub> on CaCO<sub>3</sub> surfaces under dry and wet conditions” by H. J. Li et al.***

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We would like to thank the reviewer for the constructive suggestions to improve our manuscript. We have implemented all the comments and suggestions in the revised manuscript. Below please find a detailed point-by-point response to each comment.

1. The manuscript repeatedly mentions that SEM analysis of the particles was performed (e.g., Abstract line 10; page 7118, line 21; page 7119, line 7). However, no details are given in the experimental section and no data/results are presented. The authors assume a cubic shape for CaCO<sub>3</sub> particles, which becomes important for calculating the uptake coefficient at higher RH. An SEM image should be included in the

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supplemental information and discussed in relation to the assumed cubic shape.

Response: The SEM image of  $\text{CaCO}_3$  is provided in the revised manuscript. We have also measured the size distribution of grinded  $\text{CaCO}_3$  particles using a laser particle sizer; based on this result, we calculated the surface area of  $\text{CaCO}_3$  to be  $0.19\text{m}^2/\text{g}$ , we used this value in the discussion of the revised manuscript.

2.The authors calculate that 3.4-3.6% of the oxygen atoms correspond to  $-\text{Ca}(\text{OH})$  sites (page 7120, line 26). Since XPS analyzes the bulk sample, it would be more insightful to estimate the percentage of surface sites corresponding to  $-\text{Ca}(\text{OH})$  sites versus  $-\text{Ca}(\text{CO}_3\text{H})$  sites.

Response: The X-ray of XPS could only penetrate into about 10 nm depth of particles, hence the results of XPS reflects the composition information of particles surface, not the bulk sample. The XPS shows the oxygen atom ratio of  $\text{Ca}(\text{OH}):\text{CaCO}_3$  is 100:7.3, unfortunately with this technology we could not separate  $\text{CaCO}_3$  and  $-\text{Ca}(\text{CO}_3\text{H})$ .

3.The  $\text{NO}_2$  concentrations used in these experiments are orders of magnitude higher than found even in the most polluted regions ( $4.81 \times 10^{15}$  to  $1.22 \times 10^{16}$  molecules  $\text{cm}^{-3}$  for  $\text{RH} < 10\%$  versus  $5 \times 10^{12}$  molecules  $\text{cm}^{-3}$  in extremely polluted regions and more typically  $2 \times 10^{11}$  molecules  $\text{cm}^{-3}$ ). This significant difference should be acknowledged and discussed in the paper. This also has great implications for the low RH studies, in which the authors conclude that  $\text{N}_2\text{O}_4$  is the reactive species. The concentration of  $\text{N}_2\text{O}_4$  in their experiments is never calculated – yet they range from  $5.7 \times 10^{12}$  to  $3.7 \times 10^{13}$  molecules  $\text{cm}^{-3}$ , which is considerably higher than equilibrium concentrations at tropospheric levels ( $1 \times 10^4$  molecules  $\text{cm}^{-3}$  in remote regions and  $6 \times 10^6$  molecules  $\text{cm}^{-3}$  in extremely polluted regions). If uptake coefficients were calculated for  $\text{N}_2\text{O}_4$  at low RH, does this reaction likely compete with  $\text{HNO}_3$ ?

Response: We agree that the  $\text{NO}_2$  concentration used in the laboratory is higher than that in the real atmosphere. To meet the detection limit of the instrument (DRIFTS), we have to use this level of  $\text{NO}_2$  concentration in the laboratory experiments. We

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addressed this difference in the revised manuscript. When discussing the implication of the laboratory results to the atmospheric chemistry, we have pointed out: 1) the reaction with  $\text{N}_2\text{O}_4$  is only happened under dry condition, under this condition,  $\text{NO}_2$  reaction is not as important as  $\text{HNO}_3$  in the troposphere; 2) under wet condition,  $\text{NO}_2$  reacts directly on the surface and no  $\text{N}_2\text{O}_4$  is needed, the importance of the reaction of  $\text{NO}_2$  on  $\text{CaCO}_3$  particles in the troposphere is comparable to that of  $\text{HNO}_3$ .

4. Figure 1. It appears that the black squares (left axis) and open circles (right axis) are the same data with the left and right axes scaled differently, making the data redundant. The right axis should be scaled to correlate with the left, thus requiring only one set of data points. The line appears to be arbitrary; instead, the authors should include the BET best fit line. The authors should also review 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, 2005. This article presents an extensive discussion of surface adsorbed water that the authors should consider in their discussion.

Response: In the revised manuscript, this figure will be used as supporting information. The data are from the same data, but the two axis have different meaning, the left axis is based on directly measurement of infrared absorption, the right axis is the number of water monolayer based on BET fit results. With the right axis we could better describe the relationship between RH and the number of water monolayer.

5. Figure 2 and Figure 10. It appears that these two figures present the same data, merely plotted using different variables (although Fig. 2 has one less data point). This presentation is redundant. I suggest eliminating Figure 10 and moving Figure 2 along with its discussion (page 7121, line 13 through page 7122, line 7). The effect of surface adsorbed water on the reaction with  $\text{NO}_2$  might fit more naturally after Section 3.3.

Response: Figure 2 and Figure 10 are based same dataset, but have different meaning. The figure 2 is to describe the influence of water vapor on reaction rate; this is

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helpful for the discussion on reaction mechanism, while Figure 10 discuss the impacts of RH on uptake coefficient.

6. Figure 4 and page 7123, lines 20-24. These plots appear to follow normal saturation curves consistent with the formation of a “passivation layer,” where calcium nitrate products remain immobile and unreactive. Such plots could be fit with an appropriate saturation model; thus, the benefits of dissecting these kinetic plots into three regions remain unclear.

Response: Figure 4 shows the nitrate production rate, not the absorption rate of NO<sub>2</sub>. The nitrate production rate is the results of multi-steps. Based on the measurements, we believe that the reaction mechanism and reaction order were changing during the reactions processes. At the initial stage, the absorption of NO<sub>2</sub> was the rate determining step, one can use normal saturation curves; however, at the third stage, formation of the reactive surface sites was the rate determining step. Based on this reason, we could not simply use saturation curves to fit the results.

7. Figure 5. When calculating  $\ln\{d\text{NO}_3-/dt\}$  for region I of the  $4.81 \times 10^{15}$  molecules cm<sup>-3</sup> data set, were all data points between 0 and 50 minutes used? Clearly the number of reactive surface sites is decreasing during this time period as evidenced by the saturation behavior. Given this observation, it would be best to fit the initial linear portion (e.g., 0 – 15 minutes) of this data to determine  $\ln\{d\text{NO}_3-/dt\}$ . This analysis, however, would increase  $\ln\{d\text{NO}_3-/dt\}$  for the first two data points in Figure 5, resulting in a lower slope. Such an analysis might significantly challenge the concluded second order w.r.t. NO<sub>2</sub> for this reaction, which is already a stretch based on the slope  $1.63 \pm 0.23$ . Given the uncertainty in this analysis, I am greatly concerned by the strong mechanistic conclusions presented for low relative humidity. The authors need to carefully consider the interpretation of their data, and should revisit this analysis and their mechanistic conclusions.

Response: We agree with the reviewer’s comment. In the revised manuscript, we

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carefully re-analyzed the results, added one point, used the slope of the initial linear portion (e.g., 0-10 minutes) of this data to determine  $\ln\{d\text{NO}_3-/dt\}$ , and we obtained a slope of  $1.69 \pm 0.19$ .

8. Figure 6. Why are Kulbelka-Munk units used in this figure? Why are absorbance units used everywhere else? Although Kulbelka-Munk units theoretically apply to diffuse reflectance spectroscopy, several studies note the utility of absorbance units for adsorption studies and heterogeneous reactions. The authors should be consistent with the presentation of their data or they should include a discussion in the text explaining any differences.

Response: We agree with the reviewer's comment. In the revised manuscript, we changed the figure with absorbance units.

9. Figure 7 & Figure 8. Nitrate formation in Figure 8 appears linear for the  $\text{NO}_3-$   $\nu_1$  peak at  $1048\text{ cm}^{-1}$ . The analysis in Figure 7 suggests saturation behavior for the  $\text{NO}_3-$   $\nu_3$  peak at  $1344\text{ cm}^{-1}$ . Why is there a discrepancy? It is also very interesting to note that the surface adsorbed water levels off after 30 minutes, especially since calcium nitrate is of interest given its hygroscopic properties.

Response: In Figure 7 we would like to illustrate the formation of  $\text{NO}_2-$ , so we did not display the  $\text{NO}_3-$   $\nu_1$  peak at  $1048\text{ cm}^{-1}$ . The  $\text{NO}_3-$  absorption at  $1688\text{ cm}^{-1}$  is overlapped with that of  $\text{H}_2\text{O}$  at  $1636\text{ cm}^{-1}$ , Gaussian peak fitting was used and thus has high uncertainty. In the revised manuscript, we used an IR spectrum with full scale. The water absorption at  $3000\text{--}3600\text{ cm}^{-1}$  shows clearly increasing trend. The  $\text{NO}_3-$   $\nu_3$  peak at  $1344\text{ cm}^{-1}$  is overlapped with the  $\text{CO}_3^{2-}$  absorption at  $1380\text{--}1560\text{ cm}^{-1}$ , so the  $\text{NO}_3-$  absorption at  $1048\text{ cm}^{-1}$  is more reliable for concentration analysis. In the revised manuscript, we used  $1048\text{ cm}^{-1}$  for  $\text{NO}_3-$  concentration both in Figure 7 and 8.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 7115, 2009.

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