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Atmospheric
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Discussions

Interactive comment on “Kinetics and mechanisms of heterogeneous reaction of NO$_2$ on CaCO$_3$ 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.

General Comments: This experimental study on the interaction of NO2 with CaCO3 substrates is certainly of interest to the atmospheric community although the results seem to indicate that the importance of this reaction will likely be very limited in view of its low rate at atmospherically relevant concentrations of NO2. In this respect this disproportionation reaction is no different from its variant in aqueous solution, and the

interesting aspect of HONO formation in the gas phase has not been addressed quantitatively owing to limitations imposed by the used experimental technique (DRIFTS). A quantitative comparison with an “inert” substrate material such as CaSO4 would have been very informative in this regard in addition to the spectral reference discussed on pg. 7122, line 24-25. It seems that the used CaCO3 “surface” is only the solid support for the reaction of NO2 with adsorbed water, and the question arises if calcite could be replaced by any other mineral substrate. Like for calcite, most if not all mineral substrates are also terminated by OH-groups.

Response: We have studied the reaction of NO2 with an “inert substrate”, SiO2, under the same condition as with CaCO3, and we could not detect NO3- formation. CaCO3 is different from an “inert” substrate, because: 1) it is alkaline and can react with nitric acid to form nitrate; 2) Ca(NO3)2 has strong hygroscopic property and could reach to deliquescence point at very low RH, this will help to expose CaCO3 to HNO3 until CaCO3 is fully reacted.

1. Pg. 7119, lines 9-12, the “specific geometric surface” is calculated from a “mean”dimension of the cubic CaCO3 crystallites of 5.6 micron. In order to obtain the correct value one must take into account the measured particle size distribution (PSD) of the ground particles in the 1-10 micron range because each size bin must be properly weighted in order to obtain a meaningful average surface area that may be compared to a BET measurement. The small sizes will in general contribute much more to surface area than the larger ones, depending on the PSD. Another way would be to sieve a certain fraction and perform the surface area measurement on this fraction. What are the definitions of the terms “specific geometric surface area” (line 11-12) and “specific surface area” (line 27-28)? In the context of heterogeneous reaction kinetics the geometric surface area is neither of the two above. It usually pertains to the surface area of the sample support.

Response: We agree with the reviewer’s comment. In our revised manuscript, we at first define the term of these areas, using ABET for BET measures surface area; Ap for geometric surface area of particles calculated from microscopic size of cubic shape; and AS for geometric area of the sample holder in Knudsen Cell. We did measured the size distribution of grinded $CaCO_3$ particles using a laser particle sizer; based on this size distribution, we calculated the surface area of $CaCO_3$ to be 0.19m2/g. this value is slightly smaller that of 5.6 micron $CaCO_3$ crystallites, and is used in the discussion of the revised manuscript.

2.Pg. 7119. lines 18-21: What is the flow lifetime in the DRIFTS cell?

Response: The flow lifetime in the DRIFTS cell is 2 seconds.

3. Pg. 7120, lines 19 and following, as well as throughout the text: Regarding the presence of surface OH-groups the authors cite all the appropriate references. However, I believe that they misinterprete the results: Once you cleave a calcite single crystal in vacuum in the presence of minute amounts of H_2O vapor the surface reconstructs and converts essentially into an interface of average composition $Ca(OH)(HCO_3)$ that reacts with atmospheric trace gases. There is no experimental proof of reversibility of OH-surface termination as claimed in reacton R2 or reaction with additional adsorbed water. This is pure speculation by the authors and not supported by any evidence, unless I am missing something. As a function of relative humidity (rh) there is more or less strongly and weakly-bound water adsorbed on top of this OH- and HCO_3-terminated surface layer. Santschi has quantitatively described the H_2O adsorption on ground calcite which is the substrate the authors use in the present work (C. Santschi et al., J. Phys. Chem. A 2006, 110, 6789-6802

Response: We agree with the reviewer's comment, the reverse of reaction R2 is just speculation. In the revised manuscript we have deleted this reaction and the associated discussion.

4. Pg. 7120 or 7121: What are the results of the reference measurement NO_2 + H_2O + empty sample support? Did the authors properly substract the "background" in case there is one?

Response: With DRIFTS, we need to have particle samples to measure the diffusive reflectance of IR. We could not do it with an empty sample support. The "background" suggested by the reviewer can be measured with SiO_2 in the sample support, with which we did not detect nitrate formation.

5.Pg. 7121, line 9-10: What metric did the authors take to establish a "monolayer" of adsorbed H_2O at 52% rh? The measured BET (4.91 m2g-1) or the calculated value of 0.37 m2g-1 based on an average dimension inspected by eye? How many molecules of adsorbed H_2O cm-2 is a monolayer?

Response: the reference by Goodman et al. describes how to calculate the number of water monolayer. It was based on BET fit to get IR absorbance of a monolayer of water, then based on lab measured the IR absorbance of water, on can calculate the number of monolayer of water.

6. How does the rate law discussed on pg. 7121, line 23 to 25 and displayed in Figure 2 look for different values of $[NO_2]$? What the authors present is perhaps a rate coefficient and its associated dependence on $[H_2O]$, but a rate law always explores the concentration dependence of all reaction partners within a certain range. This question is justified because of the apparent complex reaction mechanism and its complicated dependence on $[NO_2]$ and $[H_2O]$ (see below). The authors do not have a clue as to the formation of additional "active sites" on the surface as claimed on pg. 7121, line 28. What is the evidence?

Response: The Figure shows nitrate formation rate at a fix NO_2 concentration (6.88×1015 molecules $cm-3$) and different water vapor concentrations. It is to illustrate the impacts of water vapor on the reaction rate; this is helpful for reaction mechanism discussion. To avoid confusion, in revised manuscript, we added NO_2 concentration in Figure 2.

7. 7. Pg. 7124, line 8-10: I take issue with the statement that the data for stage I disclose a second order rate law. The first data point on the left in Figure 5 is at $\ln[NO_2]$

= 36.45 which does not correspond to the lowest [NO2] given in Figure4. Instead, this value should be at ln[NO2] = 36.1 corresponding to [NO2] = 4.81x1015 molecule cm-3. Assuming that this "reanalysis" is correct, I conclude that there is no straight line, neither in Figure 5 nor in Figure 9. In both cases there is distinct curvature that is apparent beyond the uncertainty of the individual data points. This is especially apparent in Figure 9. This means that the rate law is more complex than the authors think and that there is no simple linear relationship in the doubly logarithimic plot. In addition, for both analyzed cases, low and high rh, the range seems to be way too small for the derivation of a rate law: a factor of roughly 2.5 (Figure 4) and 3 (Figure 8) for low and high values of rh, respectively. It is simply impossible to derive a rate law over that narrow a concentration range!

Response: We are thankful for this comment. We lost one data point when transferring the data between different files. This mistake is corrected in our revised manuscript. We carefully re-analyzed the results, added the lost data point. Then, as suggested by the reviewer, we used the slope of the initial linear portion (e.g., 0-10 minutes) to determine ln{dNO3−/dt}, and we obtained a slope of 1.69±0.19, this also shows high precision of the experimental results. We agree that the NO2 concentration range is narrow; however, this should not prevent us from discussing the reaction law, as long as we do not try to generalize the results outside this range of NO2 concentration. If future experimental conditions allowed, we would like to expand the range of NO2 concentrations for rate law determination.

8. The authors prefer to normalize the rate of initial uptake (Figure 10: Where are the experimental uncertainties or vertical error bars?) to the BET surface. Although the total internal and external surface area is eventually probed by NO2 it is more reasonable to base the uptake coefficient on the geometric surface rather than the BET or the calculated total internal and external surface that the authors call "specific geometric surface area", whatever that is (see point 1 above). Although the authors concede on pg. 7128, line 2-4, that the available surface area should be close to the

geometric surface area at short reaction times, it is NOT the geometric surface area that they use! In the case of Mertes and Wahner (1995, referenced) the geometric surface area of the aqueous surface was taken in order to obtain numbers on the order of 10-4 for the mass accommodation coefficient alpha which is an upper limitng value for gamma, the uptake coefficient. Only if they normalize the rate to the geometric surface area they are able to compare their results to Mertes and Wahner. From the work of Wagner et al. (C. Wagner, F. Hanisch, N. Holmes, H. de Coninck, G. Schuster and J.N. Crowley, Atmos. Chem. Phys. 8, 91-109 (2008)) it becomes clear that the geometric surface area is a superior normalization factor compared to the BET surface area because the ïA^{2}gÂć values obtained in a low pressure flow reactor (using the geometric surface area) are a factor of three SMALLER than the atmospheric pressure aerosol flow tube results. The ïA^{2}gÂć values obtained using the BET-based surface area are roughly three to four orders of magnitude smaller than the ones based on the geometric surface area. The conclusion is that it is unreasonable to normalize initial uptake rates of gases interacting with sample powders by BET surfaces as it may result in unrealistically low gamma values. The comparison of Wagner et al. is most instructive in this respect.

Response: in the revised manuscript, we compared our results with Wagner et al. When calculating the uptake coefficient, to use which surface area is always debatable. In order to compare with the literature results, we used BET surface area. And we also realized that in many occasions, we should consider to use geometric surface area. The problem is, we can use different method to estimate geometric surface area, but we don't have a reliable method to obtain accurate value of geometric surface area.

9. Pg. 7128, lines 7-11: These statements are unsupported by data and merely reflect the authors belief without a firm experimental basis. They are untenable as such.

Response: We have the experiment evidence (gama = (0.84±0.44) ×10−6) to discuss the implication of the reaction in the troposphere. We think these statements fit more in the section of discussion than in the results, so we moved this sentence into the discussion section of the revised manuscript.

10. Regarding the Discussion on pg. 7128-7133 the above criticism obviates much of the discussion which is a curious mix of already known chemical processes such as reactions R3 and R4 and unsubstantiated assertions such as the statement ": : :the dissociation of water by oxygen vacancy and this seems to be the rate determining factor for the reaction". This is certainly NOT the case as there is no evidence that surface reconstruction on calcite depends on atmospheric levels of water vapor (see above). Rather, these surface functional groups preexist as pointed out above (see Santschi reference). In addition, there are unbalanced equations such as equation R5 and plainly incomprehensible statements such as on pg. 7130, line 5. Because the mechanistic discussion hinges on the discovery of first- and second order rate laws for which there is no evidence, it is incumbent on the authors to completely recast their discussion.

Response: We are thankful for this comment. In the revised manuscript, we have rewritten the discussion section. The reverse reaction of R2 is deleted, R5 is balanced, and as suggested by the reviewer, we used the slope of the initial linear portion (e.g., 0-10 minutes) to determine ln{dNO3−/dt}, and we obtained a slope of 1.69±0.19. We agree that the NO2 concentration range is narrow; however, this should not prevent us from discussing the reaction law, as long as we do not try to generalize the results outside of this range of NO2 concentration.

11.The reference to adsorbed H2CO3 on pg. 7125, line 2, equation R8 (pg. 7131) and line 1-2 on pg. 7132 is misplaced. It is highly unlikely that CO2 is stored as adsorbed H2CO3 in the presence of water because the heat of adsorption of H2O is larger than the kinetic barrier to H2CO3 decomposition to CO2 and H2O(ads). At least all DFT calculations point into that direction, and the experimental evidence for adsorbed and stable carbonic acid (over days!)is weak or non-existent

Response: We agree with the reviewer's comment. Here adsorbed H2CO3 is treated

as an intermediated and will dissociate to CO2 and H2O, e.g. R9. In our revised manuscript, a reference about this (Al-Hosney and Grassian 2004) is listed.

12.The first six lines of the Abstract represent background information and should be deleted.

Response: Accepted.

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