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Interactive comment on “Kinetics and mechanisms of heterogeneous reaction of NO₂ on CaCO₃ surfaces under dry and wet conditions” by H. J. Li et al.

Anonymous Referee #2

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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

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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.

However, the paper cannot be published in its present form because of wide-spread errors, unbalanced chemical equations, pervasive confusion and unwarranted mechanistic speculation that is not supported by evidence whatsoever. The interested reader of Atmospheric Chemistry and Physics will be grateful for a complete overhaul of the presentation as well as a substantial change in conclusions more in line with the obtained experimental results as further explained below. The sequence of discussion follows the order of appearance in the text.

1. Pg. 7119, lines 9-12, the “specific geometric surface” is calculated from a “mean” dimension of the cubic CaCO_3 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.

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

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 misinterpret the results: Once you cleave a calcite single crystal in vacuum in the presence of minute amounts of H_2O vapor the surface reconstructs

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and converts essentially into an interface of average composition $\text{Ca}(\text{OH})(\text{HCO}_3)$ that reacts with atmospheric trace gases. There is no experimental proof of reversibility of OH-surface termination as claimed in reaction 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).

4. Pg. 7120 or 7121: What are the results of the reference measurement $\text{NO}_2 + \text{H}_2\text{O}$ + empty sample support? Did the authors properly subtract the “background” in case there is one?

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 ($4.91 \text{ m}^2\text{g}^{-1}$) or the calculated value of $0.37 \text{ m}^2\text{g}^{-1}$ based on an average dimension inspected by eye? How many molecules of adsorbed H_2O cm^{-2} is a monolayer?

6. How does the rate law discussed on pg. 7121, line 23 to 25 and displayed in Figure 2 look for different values of $[\text{NO}_2]$? What the authors present is perhaps a rate coefficient and its associated dependence on $[\text{H}_2\text{O}]$, 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 $[\text{NO}_2]$ and $[\text{H}_2\text{O}]$ (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?

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 $\ln[\text{NO}_2] = 36.45$ which does not correspond to the lowest $[\text{NO}_2]$ given in Figure 4. Instead, this value

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should be at $\ln[\text{NO}_2] = 36.1$ corresponding to $[\text{NO}_2] = 4.81 \times 10^{15}$ 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 logarithmic 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!

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 NO_2 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 α which is an upper limiting value for γ , 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 γ 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 γ values obtained using the BET-based surface area are roughly three to

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Interactive Discussion

Discussion Paper



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.

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.

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.

11. The reference to adsorbed H_2CO_3 on pg. 7125, line 2, equation R8 (pg. 7131) and line 1-2 on pg. 7132 is misplaced. It is highly unlikely that CO_2 is stored as adsorbed H_2CO_3 in the presence of water because the heat of adsorption of H_2O is larger than the kinetic barrier to H_2CO_3 decomposition to CO_2 and $\text{H}_2\text{O}(\text{ads})$. 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.

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

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

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