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Atmospheric
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Discussions

Interactive comment on “DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust” *by* M. Ullerstam, et al.

Anonymous Referee #2

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Report on " DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO2 and NO2 on mineral dust " by M. Ullerstam, M. S. Johnson, R. Vogt and E. Ljungström

This is an interesting paper that explores a novel substrate regarding a long-standing problem of the heterogeneous NOx/SO2 interaction that was hotly debated a few years ago. The title reaction takes on a new significance in relation to the effect of atmospheric particles on global climate change, a well-recognized problem whose answer is fraught with large uncertainties. The paper presents a dual-diagnostic study on the chemical kinetics of the heterogeneous interaction of NOx/SO2 using a Knudsen reactor and a DRIFTS cell. Multi-diagnostic studies such as this one should in general be encouraged because the result exceeds the sum of both components. After appropriate amendment of the points discussed below I find this work appropriate for publication in Atmospheric Chemistry and Physics as I think it will garner substantial

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interest within the community of atmospheric scientists. Here are a few points that need clarification or modification: - Regarding the formalism of the pulsed valve experiments presented on page 4076: I do not understand equation (5). How is s defined? The authors were correct in their first submission to ACPD in that the decay constant of interest, ku is simply the difference between kKC+s - kKC. The decay rate constant for the reference (no sample or sample covered) is equal to ke. It's value is needed, whether experimental (preferred) or theoretical. Attention to loose language: First §: k is a rate CONSTANT and not a rate! - The so-called "linear mass dependence" of g for which there is no theoretical justification so far (Grassian and coworkers) should be tested using steady-state rate constants obtained in the 2 mm reactor because that is where the expected multilayer interaction is expected to be largest. The lifetime of NO2 or SO2 is not long enough in pulsed valve experiments to explore deeper layers of the sample. However, my biggest problem with the present data interpretation of gapparent has to do with the fact that the data do not go to sufficiently high masses in order to see the trend towards saturation of g. What is the number of sample layers at 120 mg? From my experience with mineral dust samples all the data displayed in Figure 3 could be below one formal sample layer. On this account it is clear that one observes a trivial linear mass dependence because the projected surface area of the sample is less than the surface area of the sample holder. It is necessary to obtain one data point at 500mg of sample in order to evaluate the saturation of gapparent. A way out of this question would be to state that the g values obtained on the basis of the BET internal surface area are lower limits to the "true" uptake coefficient. By the way: Did the authors use a mixture of NO2 and SO2 in the pulsed valve experiments of Figure 3? The text (pg. 4077) is not quite clear on this. - Pg. 4077, last §: Are the losses of SO2 and NO2 independent of flow rate? They should as the authors clearly show that a first order rate law applies. - Pg. 4078: The rate d[SO4 2-] / dt is the rate of sulfate formation and NOT the rate of reactive collisions of SO2 with the surface that are unobservable in this experiment. Regarding the sulfate expressions: exponent 2- or -2? - Page 4079: A brief discussion of the role of Surface-Adsorbed Water (SAW)

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would be appropriate. Is there SAW on the present mineral dust samples? If yes, how much? How determined? - Pg. 4080: Are there any indications of NO evolution following Reaction 3? Could some of the nitrite observed by DRIFTS be due to the primary reaction R3? The authors do not make it sufficiently clear on what basis they are able to attribute nitrite formation to Reaction 1 and exclude nitrite formation in Reaction 3. On other substrates HONO formation has been observed resulting from heterogeneous NO2/SO2 interaction. - Pg. 4080, end of first §: The rate-limiting step is always the slowest one, so that the authors would be unable to measure the kinetics of the rate of physisorption in these experiments. The uptake of SO2 can not possibly be controlled by the rate of physisorption at g = 5x10-6 unless I misunderstand. - Pg. 4081: I do not believe that much SO2 is taken up into an aqueous sulfate layer owing to the small solubility of SO2, unless the layer is at high pH! Is it? - Pg 4082: There is confusion between the uptake coefficient and the mean free path: the first g encountered in the text after equation 12 must be l. - I would strongly suggest to add the following to Table 1: Values for ke for 11 and 2 mm escape apertures as well as w (gas-reactive substrate collision frequency). This enables the reader to independently evaluate the presented kinetic results.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4069, 2003.

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