

Interactive comment on “Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate” by L. Li et al.

L. Li et al.

Received and published: 7 April 2006

The reviews of the referees are highly appreciated. Below are the discussions and revisions made according to the comments.

— REPLY TO COMMENTS BY REFEREE #2 —

GENERAL COMMENT 1: The general concern is that while the title states that kinetics and mechanism for the sulfur dioxide oxidation by ozone are being explored, in the end the conditions during the experiments were such that the actual reaction of ozone with adsorbed sulfite was not the rate limiting step. From that perspective I suggest to formulate abstract and title a little more cautious and to more emphasize the evidence

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

found for the mechanistic aspects. REPLY: The title has been changed into “Mechanistic study of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate” to emphasize the evidence found for the mechanistic aspects in the revised version.

GENERAL COMMENT 2: In the kinetic analysis section, the authors could derive lower bounds for the kinetics of the surface reaction. This aspect might also affect the atmospheric implications section, as eventually the oxidation step itself could also become the rate limiting process, depending on the gas phase concentrations of both ozone and SO₂ in the atmosphere. REPLY: In the present article, we intend to deduce the mechanisms by the experimental evidences. The present experimental results cannot provide enough evidence that the oxidation step itself becomes the rate limiting step in concentration ranges of 2 - 40 ppm of SO₂ and 5 - 50 ppm of O₃ respectively. Unfortunately, the DRIFTS in our lab cannot be used to explore the reaction processes in lower concentration than ppm level because of detect limitation of the DRIFTS. At this moment, we are not sure that the oxidation step itself might become the rate limiting process if the concentrations of reactants decrease to the atmospheric levels. But the concentration ratios of SO₂/O₃, O₃/particle and SO₂/particle in our experiments are in similar magnitudes to the atmospheric values, we expect that the experiment results can provide an estimation of reactive uptake coefficient used in air quality model.

GENERAL COMMENT 3: Another general aspect might to mention and consider the fact that while CaCO₃ is indeed an important dust constituent for certain sources; many dust aerosol types do not contain a lot of CaCO₃. REPLY: For choosing CaCO₃ as sample particles, our intention is: First, CaCO₃ is a constituent of the mineral dust. Especially for example, in North China, CaCO₃ is a major component of the atmospheric dust, resulting in an alkalescence of dust. In high particle pollution of North China, heterogeneous conversion of SO₂ on CaCO₃ surface might be very important for SO₂ removal and secondary aerosol formation. Second, it is difficult to obtain a detailed reaction mechanism on the mineral dust in which the compositions are very

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

complex. Goodman et al. (2001) studied the heterogeneous uptake of SO₂ on simple constituents, i.e., Al₂O₃ and MgO particles, in which Al₂O₃ was characterized as acidic oxides and MgO as basic oxides. In the present article, we chose CaCO₃ to explore some insights into the mechanisms of heterogeneous reactions to represent the total mineral dusts for its alkalescency. The uptake coefficient on CaCO₃ determined by us is of the same order of magnitude as that on the mineral dusts determined by other researchers.

SPECIFIC COMMENTS:

COMMENT: The abstract contains too much introductory material; this should be reduced to a minimum. REPLY: The abstract has been shortened by deleting the excess introductory materials in the revised version.

COMMENT: P581, L7: specify the 'special' chemical properties (hydrate formation, others?). Also note that hydration occurs also in other mineral, but slower. REPLY: The hydration occurs on the surface of CaCO₃, which results in an alkalescent surface. As the referee pointed out, the hydration also occurs on other mineral constituents. We intend to indicate that CaCO₃ is alkalescent and is a carbonate, different from many other constituents of dust. The term 'special' has been deleted in the revised version to avoid misunderstanding.

COMMENT: P581, L25: Recent work by Hoppel et al. in J. Geophys. Res. might be added. REPLY: The work has been referred in the revised version.

COMMENT: P583: In order to understand how this experiment works, one should emphasize that the gas flow was forced through the powder, which seems to be the case based on the Figure. In relation to that point, the reader should learn what the probing depth of the IR beam is approximately: does it explore the uppermost few layers or rather the entire sample? REPLY: The fact that the gas flow was forced through the powder has been added to the revised version. The probing depth of IR beam was estimated as less than 0.2 mm of the powder layers in our reactor. Only the

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

uppermost layers of the powder are explored by IR.

COMMENT: P584: I wonder what happened when in absence of ozone SO₂ was switched off. How much sulfite would have disappeared again? According to the text, ozone has been added at the moment SO₂ has been switched off. Depending on the life time for desorption compared to that for reaction, the coverage by SO₂ may not have been well defined. In addition, the time needed to equilibrate the signal with SO₂ alone determined by the adsorption / desorption kinetics or by mass transport across the sample (to coat all the internal surface area). A switching on-off cycle of SO₂ alone would help to clarify this. REPLY: We have carried out an experiment similar to the referee's suggestion. The result showed that sulfite on CaCO₃ cannot disappear in absence of ozone. Unlike SO₂, which is physisorbed on the surface, sulfite and sulfate are chemisorbed on the surface and cannot be removed upon evacuation. Goodman et al. (2001) studied the heterogeneous uptake of SO₂ on Al₂O₃ and MgO particles. They pointed out when SO₂ was physisorbed on the surface, two small peaks at 1149 and 1330 cm⁻¹ became apparent in the IR spectra and these two peaks disappeared after evacuation. In our experiments, two bands at 1149 and 1330 cm⁻¹ of SO₂ were not visible before and after evacuation because of SO₂ signal was in the level of noise under ambient conditions, however, the band at 900 cm⁻¹ attributed to the vibration of sulfite did not changed after evacuation, thus it is deduced that the sulfite cannot be removed upon evacuation.

COMMENT: P584, L5: this probably indicates that O₃ just undergoes reversible adsorption in absence of a reactant. REPLY: We agree that this probably indicates that O₃ just undergoes reversible adsorption in absence of a reactant. The IR band of O₃ on CaCO₃ has not been detected under our experimental conditions, this probably means that the concentration of O₃ absorbed on the surface of CaCO₃ is very low.

COMMENT: P586, last paragraph: not that a reactive collision is not a well defined quantity. I would define the reaction probability as rate of product formation normalized to the collision rate of SO₂. The problem is that the uptake coefficient of SO₂ may

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

be much larger at times, especially at the beginning, before the reaction quasi steady state is reached that is considered here. REPLY: We have modified the definition of uptake coefficient according to the Referee's comment.

COMMENT: P587, L15: is it important for this calibration that the two mixed powders have the same surface to volume ratio, because the DRIFTS basically probes the internal surface? REPLY: CaCO_3 and CaSO_4 samples were ground respectively to a certain distribution of particulate diameters, and then calibration samples were obtained by mixing properly these two kinds of powders. The surface to volume ratios of these two particles was controlled to be similar at the step of grinding.

COMMENT: P588: Two issues seem appear from the reported uptake coefficients. A. Does using the term 'initial' uptake coefficient make sense in this context? Usually this term is used in experiments, in which the loss probability of the first collisions can really be resolved. It could well be that in these experiments the value of the uptake coefficient in the beginning is given by mass transport into the sample. B. Related to my questions regarding the probing depth of DRIFTS I wonder whether normalizing to the geometric surface makes sense at all in this context. The discussion around using the geometric versus the BET surface areas in analyzing Knudsen cell data are always related to a discussion of the probing depth, which is not the case here, as DRIFTS probably probes the entire BET surface? REPLY: A. The term 'initial' uptake coefficient used in the DRIFTS experiment is somewhat different from that used in the Knudsen Cell experiment because of their different time resolutions, i.e., the time resolution of the former is less than that of the latter. Thus, one can investigate the more 'initial' uptake of a reactant when using a Knudsen Cell than when using a DRIFTS reactor. The 'initial' uptake coefficient in the present paper is a reactive one, which is obtained by determining the formation concentration of a product. Considering the fact that the term "initial uptake coefficient" has been used in many related works (e.g., Usher et al., 2003; Rossi, 2003; Grassian, 2001), we intend to follow this conventional term in the present paper, though this term is not so suitable when a DRIFTS reactor is employed.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

B. In the experimental simulation studies, the uptake coefficients are usually given and compared based on BET area. However, the geometric surface area of the particles is usually used in the heterogeneous model studies because atmospheric models usually calculated aerosol surface area on the basis of the particle diameter. In order to compare with the results of other studies and to employ the atmospheric model, we have calculated two kinds of uptake coefficients based on BET and geometric areas respectively.

COMMENT: P588, L17: the discussion about the deposition velocity is not clear. What information can we get from the cited value, and where is that coming from, i.e. from what kind of measurement? REPLY: The deposition velocity of SO₂ was used to quantify the removal process of SO₂ by earth surface. The deposition velocities were measured by using micrometeorological methods over various types of earth surfaces. Dentener et al. (1996) included, for example, gas phase conversion and heterogeneous conversion of SO₂, and dry deposition of SO₂ in the atmospheric model to evaluate importance of various processes of SO₂. In the present article, we compared the uptake coefficient determined by our experiment with “uptake coefficient” determined by Dentener et al. based on the deposition velocity of SO₂.

COMMENT: P590, last line: how does humidity affect this comparison with rigidity? REPLY: Ravishankara (1999) proposed concepts of the terms of dynamic and rigid solids and gave several examples of these two kinds of solids in his paper. We intend to put forward a method, by comparing the initial and steady state uptake coefficients, to distinguish the kind of solids. Our experimental results indicate that the humidity has an influence on the rigidity of CaCO₃. At low humidity, CaCO₃ can be regarded as a rigid solid. At high humidity, CaCO₃ tends to act as a dynamic solid because the reactive group (reactive site) can be regenerated. However, it should be point out that the discussion about dynamic and rigid solids in the present paper is only preliminary.

COMMENT: P591, L15: I suggest introducing the hydration of CaCO₃ as a separate, explicit reaction; it is eventually the most important one, as it may determine the rate

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

of sulfite formation. REPLY: We agree that the hydration of CaCO_3 is a very important step. The hydration mechanism of CaCO_3 is not very clear, within our knowledge. Thus we have not given the CaCO_3 hydration step in the mechanism because we did not have enough data to explore hydration steps of CaCO_3 .

COMMENT: P593, L5: it should be pointed out here that just because the experimental conditions were such, that the surface reaction with O_3 was not rate determining, this does not necessarily mean that this is the case under all conditions. REPLY: Heterogeneous reaction is a complicated process which may compose of several steps. The relative importance of these steps may differ under different conditions. Our results were obtained under the specific conditions, so we should qualify the mechanisms in our article. And the conditions have been pointed out in the revised version.

COMMENT: P595: atmospheric implications: apart from the previous comment, also note that the uptake coefficient might be significantly higher at lower concentration. The interplay between relative concentrations at the surface of the dust particle will ultimately determine the removal rate of O_3 and the formation rate of sulfate. REPLY: We agree that the uptake coefficient might be higher at lower reactant concentration and concentration ratios of reactants are important to the formation rates of products on the surface of dust particle. The comments have been added in the revised version.

Other minor mistakes have been corrected and the figures have been modified according to the ACP format in the revised version.

References Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J. and Crutzen, P.J.: J. Geophys. Res. - Atmos, 101(D17), 22869-22889, 1996. Goodman A. L., Li, P., Usher, C. R., and Grassian, V. H.: J. Phys. Chem. A, 105(25), 6109-6120, 2001. Grassian, V.H.: Int. Rev. in Phys. Chem., 20(3), 467-548, 2001. Mønster, J., Rosenørn, T., Nielsen, O. J., and Johnson, M. S.: Environ. Sci. & Pollut. Res., Special Issue 1, 63-67, 2002. Ravishankara A.R. and Longfellow C.A.: Phys. Chem. Chem. Phys., 1, 5433-5441, 1999. Rossi, M.J.: Chem. Rev., 103, 4823-4882, 2003. Usher, C.R.,

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Major comments:

COMMENT: 1) These are challenging experiments in the sense that to observe the process requires high concentrations. These high concentrations can push the chemistry into a different regime. For example, it is possible that with the high concentrations of O₃ used, the rate is independent of O₃ due to surface saturation, but that in the atmosphere where concentrations are ~ 100X's lower, the rate may be linear in O₃. The authors should add a bit more in terms of qualifying their conclusions with regard to the applicability of their mechanism to the atmosphere and whether this chemistry actually happens at an appreciable rate in the atmosphere. REPLY: As far as we know, most experimental simulation studies involving atmospheric chemistry face the same problem of the low concentrations of trace gases in the atmosphere (Vogt et al., 1994; Kalberer et al., 1999). It is difficult to achieve such low concentrations of ambient condition in the DRIFTS reactor. But the reactants concentration ratio in the stoichiometry of reactions is similar to that in the atmosphere. We have qualified our conclusions with regard to the applicability of the mechanism to the atmosphere in the revised version following reviewer' suggestion.

COMMENT: 2) Judging by Figure 8, which is largely what drives the mechanistic interpretation, the slight slope observed for steady-state measurements of the log of the rate vs. log of O₃ concentration is probably being determined by the lowest O₃ value. I would predict that if the authors used even lower [O₃], a slope of 1 might be achieved. The reproducibility of that low O₃ measurement becomes important. If it was always low, it may be an indication of transitioning from a saturated to unsaturated regime. But perhaps the authors have data to rule this out? REPLY: In Figure 8 for measurements of the log of the rate vs. log of O₃ concentration (range of 5-50ppm), the slope at initial-state stage was 0. The slope at steady-state stage approached 0 at higher

Interactive
Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

[O₃] in general, it seemed to approach 1 at lower [O₃] if we just took the two data points in Figure 8. But it is difficult to investigate the reaction at O₃ concentration lower than 5 ppm in our DRIFTS reactor, so we were not sure about the phenomenon. In the present article, we drive the mechanistic interpretation only based on the data derived from initial-state stage. The heterogeneous reaction at steady-state stage is very complicated with a lot of uncertainty; it is a problem for most of heterogeneous chemistry research.

COMMENT: 3) Along this line, it appears there's some inconsistency between the values of O₃ used in the experiments as listed in the table and as shown in Figure 8. In the table it appears that experiments were performed with $1.2 - 12 \times 10^{13}$ molec/cm³ where as the data in Figure 8 don't go below 1.0×10^{14} molec/cm³. REPLY: The O₃ concentration has been corrected as $12 - 120 \times 10^{13}$ molec/cm³ in Table 1.

COMMENT: 4) The authors raise another common problem with these experiments related to available or accessible surface area. The authors' point out that the influence of the chemical composition of the dust cannot be elucidated until this issue of which surface area to use in the derivation of the reaction probability is resolved. Moreover, meaningful comparison between results obtained with different techniques becomes difficult. There was a similar discussion on another ACPD manuscript recently. DRIFTS and Knudsen Cells operate on very different timescales and that in itself calls into question the comparison of initial uptake coefficients determined by each technique. This paper says that the best time resolution in their experiments was 40 seconds per measurement. That means 40 seconds have elapsed since the initial exposure whereas Knudsen Cell experiments typically obtain a point on the 1 second (or less) time scale. So wouldn't comparing steady-state uptake coefficients be more meaningful in this case? REPLY: Comparing of the steady-state uptake coefficients may be more meaningful, but it will raise other problems. First, there are few results about steady-state uptake coefficients for comparison; second, unlike the experimental conditions in lab, under the real atmospheric conditions the uptake is usually carried

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

out under the “initial-state”, not the steady-state, because the concentrations of trace gases are very low. Thus, we think it is suitable to compare initial uptake coefficients.

COMMENT: 5) A recent paper by Umann, et al JGR-Atmospheres vol 110, D22306 2005 showed measurements of SO₂ during dust plumes from the MINATROC II campaign. The SO₂ observations suggested that dust had no (negative) impact on SO₂ concentrations. The authors might want to at least cite this paper and offer a reason (rates too slow, not CaCO₃ rich dust, etc). REPLY: As Umann stated in his paper, the reason that the dust had no (negative) impact on SO₂ concentrations was because the dust composition possibly had a great influence on uptake of SO₂, but the paper did not indicate which component was important. We have cited the paper and have given the explanation based on the comments.

Minor Comments:

COMMENT: 1) The authors refer to the “special chemical properties” of carbonates a few times (e.g. pg 581 line 7). What are they? Basic? REPLY: The hydration occurs on surface of CaCO₃, which results in an alkalescency of surface. We intend to indicate that CaCO₃ is different from many other constituents that used in the other studies of heterogeneous chemistry. The term ‘special’ has been deleted in the revised version to avoid misunderstanding.

COMMENT: 2) The range of concentrations used in the expts should appear in the abstract. REPLY: The range of concentration used in the experiments has been added to the abstract.

COMMENT: 3) The authors refer to “different sulfates” or “different forms of sulfate” on pg 586. Are these forms known or just inferred from the different maxima in the spectral band? REPLY: The terms “different sulfates” or “different forms of sulfate” used in the paper were used to separate overlapping sulfate bands inferred from the different maxima in the spectral band. In the revised article, we only use the term of “different forms of sulfate”.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Interactive
Comment

COMMENT: 4) What is meant by H₂O being able to regenerate reactivity of CaCO₃? Does the reactivity decrease after long exposure? I didn't notice this aspect from the description of the results. REPLY: The surface reaction of SO₂ consumes reactive sites on CaCO₃ surface, resulting in a gradual decrease of reaction rate. But our experiments shows that the reaction can reach a steady state in which the reaction rate keep a constant, in other words, the number of reactive sites keeps a constant. And the steady state can last until the four-hour experiment was stopped. We think H₂O plays an important role in the steady state. The product CaSO₄, which is more hygroscopic than CaCO₃, can combine with H₂O to form CaSO₄·nH₂O. The molecular of CaSO₄·nH₂O is bigger than CaCO₃, thus the formation of CaSO₄·nH₂O can modify the surface structure and exposes new reactive sites. So H₂O regenerates the reactivity of CaCO₃ possibly through a procedure of the formation of CaSO₄·nH₂O.

COMMENT: 5) On pgs 593-4 the authors write that Li and coworkers introduced the mass transfer rate coefficient subject to equations 11 - 13. I don't see how these are any different than the Fuchs-Sutugin approach to determining mass transfer in the transition regime. A minor point, obviously, but maybe I'm not seeing the difference. REPLY: In article of Li and coworkers, the Fuchs-Sutugin approach was used to simulate the heterogeneous condensation processes. We have cited the book in the revised version.

COMMENT: 6) On pg. 594-5 the authors compare the lifetime of SO₂ by their mechanism to other gas-phase oxidation processes (OH and HO₂). Shouldn't the authors mention that the actual average lifetime of SO₂ in the absence of dust is more like 5 days due to cloud processing? REPLY: We agree that the cloud process is very important for SO₂ oxidation, and this has been discussed in the corresponding text.

References Vogt.R. and Finlayson-Pitts.B.J.: J. Phys. Chem., 98, 3747-3755, 1994. Kalberer, M., Ammann, M., Gäggl, H. W., Baltensperger, U.: Atmos. Environ., 33, 2815-2822, 1999.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper