Response to reviewer #2

We thank the reviewer for carefully reviewing our manuscript and providing helpful comments. All the comments will be addressed in the revised manuscript and we believe that the revisions based on these comments will substantially improve our manuscript. In the following please find our responses to the comments one by one, and the corresponding changes to be made to the manuscript. The original comments are shown in italics. The changes to be made in the revised manuscript are highlighted.

I support the other referee's assessment, including the recommendation that Part 1 and Part 2 be combined into a single article. The articles don't stand on their own, and studying the reaction of SO_2 *with* NO_2 *in the absence of* O_2*, as in Part 1 - since* O_2 *apparently plays a role in the reaction - is not relevant for atmospheric chemistry. I also agree that there are numerous English language errors in this manuscript.*

Response:

We appreciate the reviewer's opinion on how to better present our studies. However, these two studies are substantially different regarding the scientific questions under investigation and the chemistry involved, although they have some links. We have decided to arrange the two manuscripts as independent papers instead of companion papers to highlight their distinct features. The reasons for this arrangement are as follows:

1. The question whether the multiphase reaction of SO_2 directly with NO_2 is an important pathway for sulfate formation in the real atmosphere, e.g., during haze episodes in China, requires investigating the "pure" reaction of SO_2 with NO_2 without confounding effects of other oxidants. In another manuscript (Zhao et al., 2017), we address this question. And in this manuscript, we address a different question, i.e., whether the multiphase reaction of SO_2 with O_2 in the presence of NO_2 is an important reaction pathway of SO_2 oxidation. Both reactions have their own relevance to the atmosphere.

2. We found that the multiphase reaction of SO_2 with NO_2 and the reaction of SO_2 with O_2 in the presence of NO_2 have significantly different chemistry, with different reaction mechanisms, products, and atmospheric implications.

i. The multiphase reaction of SO_2 directly with NO_2 involves two reactants whereas the reaction of SO_2 with O_2/NO_2 involves three reactants. In the former reaction NO_2 is the main oxidant of SO_2 while in the latter reaction O_2 is the main oxidant of SO_2 and NO_2 only acts as an initiator of chain reactions.

ii. According to the reaction mechanism, the main products in the multiphase reaction of SO_2 with NO_2 are sulfate and nitrite with a stoichiometry of 1:1. In contrast, the main product in the multiphase reaction of SO_2 with O_2 in the presence of NO_2 is sulfate and the ratio of sulfate to nitrite is much higher than 1:1 because nitrite is only formed in the chain initiation step.

iii. Due to the different reaction mechanism, the atmospheric implication of the reaction of SO_2 with O_2 in the presence of NO_2 is significantly different from the direct reaction of SO_2 with NO_2 because the former leads to much faster sulfate formation and has much less influence on reactive nitrogen chemistry in the atmosphere.

Based on these reasons, we will change the title of this manuscript to "NO_2-initiated Multiphase Oxidation of SO_2 by O_2 on $CaCO_3$ Particles" in the revised manuscript. Accordingly, in the revised manuscript we will delete the parts where we stated about the companionship of these two papers (lines 63-64, 80 in the manuscript). We will also adjust the wording in the abstract and introduction to reflect this change.

Regarding the language errors, we will have a thorough language check of the text of this manuscript and correct the errors in language.

The study and the results presented are interesting. However, I have doubts about the technical soundness of the approach. For one thing, it's impossible to understand the experimental approach based on what is written in section 2 of this manuscript. Yes, the reactor was a flow reactor, but where were the particles? Were they part of the flow? Or were gases flowing past the particles which are stationary on a surface? What were the particles like (size, shape, porosity, etc.)? How were they prepared and dispersed? The manuscript is meaningless without these basic pieces of information. It is possible that they were mentioned in Part I of the manuscript, but I am being asked to review only this manuscript - and it must stand on its own at least to this extent.

Response:

Agree. In the revised manuscript, we will elaborate the experimental part. The details of experiments including the details that the reviewer is concerned with will be added and explicitly described. The revision will also reflect the change from the companion paper of our last manuscript to a completely independent paper. The revised experimental part will be as follows.

"The experiments were conducted using a flow reaction system and the setup is illustrated in Fig. S1. The experimental setup and procedure used have been described in details in previous studies (Zhao et al., 2017; Zhao et al., 2011; Liu et al., 2008). A gas mixture of NO_2, SO_2, O_2, N_2, and water vapor reacted with particles deposited on a substrate in the flow reaction cell. The concentrations of SO_2 and NO_2 were controlled using mass flow controllers by varying the flow rates of SO_2 (2000 ppm in high purity N_2, National Institute of Metrology P.R. China), NO_2 (1000 ppm in high purity N_2, Messer, Germany), and synthetic air [20% O_2 (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd.), 80% N_2 (high purity grade: 99.999%, Beijing Haikeyuanchang Practical Gas Co., Ltd.)]. Relative humidity was controlled by regulating the flow rates of reactant gases, dry synthetic air, and humidified synthetic air. Humidified synthetic air was prepared by bubbling synthetic air through fritted glass in water. In addition, in some experiments O_2 concentrations were varied by regulating the mixing ratios of O_2 and N_2 in order to investigate the effect O_2. $SO_2/NO_2/O_2/H_2O$ mixtures flew through the reaction cell and reacted with individual stationary $CaCO_3$ particles deposited on a Teflon-FEP film substrate annealed to a silicon wafer. RH and temperature were measured using a hygrometer (HMT100, Vaisala) at the exit for gases of the reaction cell. Additionally, temperature was measured using another small temperature sensor (Pt 100, 1/3 DIN B; Heraeus) in the reaction cell. All the experiments were conducted at 298±0.5 K. The experiments of this study were conducted under two RH (72% and 82%) at 75 ppm SO_2 and 75 ppm NO_2.

During the reaction, particles were *in-situ* monitored via a glass window on the top of the reaction cell using a Micro-Raman spectrometer (LabRam HR800, HORIBA Jobin Yvon) to obtain microscopic images and Raman spectra. A 514 nm excitation laser was used and back scattering Raman signals were detected. The details of the instrument are described in previous studies (Liu et al., 2008; Zhao et al., 2011). Because particles are larger than the laser spot in this study (~1.5 μm), confocal Raman mapping was used to obtain the spectra on different points of a particle in order to get the chemical information of the entire particle. The mapping area is a rectangular slightly larger than the particle and mapping steps are 1×1 μm. Raman spectra in the range 800-3900 cm^{-1} were acquired with exposure time of 1 s for each mapping point. Raman spectra were analyzed using Labspec 5 software (HORIBA Jobin Yvon). Raman peaks were fit to Gaussian-Lorentzian functions to obtain peak positions and peak areas on different points of the particle. The peak areas were then added up to get the peak area for the entire particle.

$CaCO_3$ (98%, Sigma-Aldrich, USA) with diameters about 7-10 μm on average as specified by the manufacture was used. $CaCO_3$ particles are rhombohedron crystals. X-ray diffraction analysis shows that $CaCO_3$ particles are calcite (Fig. S2). Individual particles were prepared by dripping dilute $CaCO_3$ suspended solution onto the Teflon-FEP film using a pipette and then drying the sample in the oven at 80 ºC for 10 h.

The amount of the reaction product $CaSO_4$ was quantified based on Raman peak areas and particle sizes. The details of the method are described in our previous study (Zhao et al., 2017). Briefly, the amount of reaction product $CaSO_4$ formed was followed as a function of time using Raman peak areas. Raman peak areas were converted to the amount of compound using a calibration curve obtained from pure $CaSO_4$ particles of different sizes, which were determined according to microscopic image. The reaction rate, that is, sulfate production rate, was derived from the amount of sulfate as a function of time. The reactive uptake coefficient of SO_2 for sulfate formation (γ) was further determined from the reaction rate and collision rate of SO_2 on surface of a single particle.

$$\gamma = \frac{\frac{d\{SO_4^{2-}\}}{dt}}{Z} \quad . \tag{1}$$

$$Z = \frac{1}{4} c A_s [SO_2], \tag{2}$$

$$c = \sqrt{\frac{8RT}{\pi M_{SO_2}}} \quad , \qquad (3)$$

where R is the gas constant, T is temperature, M_{SO_2} is the molecular weight of SO_2, and c is the mean molecular velocity of SO_2, A_s is the surface area of an individual particle, and Z is the collision rate of SO_2 on surface of a particle. $\{SO_4^{2-}\}$ indicates the amount of sulfate on the particle phase in mole. The average reaction rate and surface area of particles during the multiphase reaction period were used to derive the reactive uptake coefficient. The period was chosen to start after the induction period when ~10 % of final sulfate was formed. $[SO_2]$ indicates the concentration of SO_2 in the gas phase.

In addition, we carried out experiments without NO_2, on either $CaCO_3$ solid particle, or $CaCO_3/Ca(NO_3)_2$ internally mixed particle with $CaCO_3$ embedded in $Ca(NO_3)_2$ droplet in order to investigate the multiphase oxidation of SO_2 by O_2 and thus elucidate the role of NO_2 in the reaction of SO_2 with O_2/NO_2 mixture."

I suspect that the particles were not part of the flow. In which case, did the authors consider the issue of gas phase diffusion limitations in their data analysis?

Response:

Particles were deposited on a Teflon-FEP film in this study.

We evaluated the influence of gas phase diffusion on the reactive uptake coefficient using the resistor model according to the study of Davidovits et al. (2006) and references therein (see details in the Supplement S1 below, to be added in the revised manuscript). The contribution of the resistance ($1/\Gamma_{diff}$) due to gas phase diffusion to the reactive uptake coefficient in this study was less than 0.1%. Therefore we conclude that the reactive uptake of SO_2 was not limited by gas phase diffusion. The same conclusion can also be drawn by calculating the gas phase diffusion correction factor for a reactive uptake coefficient according to the method in Pöschl et al. (2007) (Equation 20 in their study).

In the revised manuscript, we will briefly discuss this point.

"The influence of gas phase diffusion on reactive uptake was evaluated using the resistor model according to the study of Davidovits et al. (2006) and references therein as well as using the gas phase diffusion correction factor for a reactive uptake coefficient according to the method in Pöschl et al. (2007). The reactive uptake of SO_2 was found to be not limited by gas phase diffusion (see details in the Supplement S1)."

The Supplement S1 to be added in the revised manuscript is as follows.

"**S1. Influence of gas phase diffusion on reactive uptake coefficients**

The Influence of the gas phase diffusion on reactive uptake coefficients was analyzed using the resistor model according to the study of Davidovits et al. (2006) and the references therein.

$$\frac{1}{\gamma} = \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sat}+\Gamma_{rxn}} \quad (1)$$

where Γ_{diff} is the transport coefficient in the gas phase, $1/\Gamma_{\text{diff}}$ is the resistance due to the diffusion in the gas phase. Similarly, $1/\Gamma_{\text{sat}}$ and $1/\Gamma_{\text{rxn}}$ are the resistance due to liquid phase saturation and liquid phase reaction, respectively. α is the mass accommodation coefficient of SO_2.

$1/\Gamma_{\text{diff}}$ can be determined using the following equation:

$$\frac{1}{\Gamma_{\text{diff}}} = \frac{0.75+0.238\text{Kn}}{\text{Kn}(1+\text{Kn})} \quad . \quad (2)$$

where Kn is Knudsen number. Knudsen number is defined as

$$\text{Kn} = \frac{\lambda}{a} \quad , \quad (3)$$

where λ is the mean free path of a molecule in the gas phase and a is the radius of the particle.

λ can be derived from

$$\lambda = \frac{3D_g}{c}, \quad (4)$$

where D_g is the diffusion coefficient in the gas phase and c is the mean molecular velocity.

c is determined by

$$c = \sqrt{\frac{8RT}{\pi M}} \quad (5)$$

where R is the gas constant, T is temperature, and M is the molecular mass of SO_2.

$1/\Gamma_{\text{diff}}$ was calculated to be 78 and $1/\gamma$ was calculated to be $\sim 8.3\times10^4$. $1/\Gamma_{\text{diff}}$ only accounted for <0.1% of $1/\gamma$. Therefore, the reactive uptake of SO_2 in this study was not limited by gas phase diffusion. The same conclusion can also be drawn by calculating the gas phase diffusion correction factor for a reactive uptake coefficient according to the method in Pöschl et al. (2007) (Equation 20 in their study, also shown as equation 6 below).

$$C_g = \frac{1}{1+\gamma\frac{0.75}{Kn}} \quad (6)$$

where C_g is the gas phase diffusion correction factor for a reactive uptake coefficient."

Was relative humidity actually measured or only inferred from mixing ratios of humid and dry air? RH is well know to be unpredictable in experiments, it should be measured directly.

Response:

Relative humidity was measured directly in our study using a hygrometer (HMT100, Vaisala). In the revised manuscript, we will clearly describe this as follows.

"RH and temperature were measured using a hygrometer (HMT100, Vaisala) at the exit for gases of the reaction cell. Additionally, temperature was measured using another small temperature sensor (Pt 100, 1/3 DIN B; Heraeus) in the reaction cell."

Line 36: This may be a language issue but it is not appropriate to refer to a point of disagreement in the literature which has prompted detailed analysis and publications as "different opinions." Replace *with "uncertainties in the pH value..." or something similar.*

Response:

Agree. In the revised manuscript, we will change “different opinions” to “uncertainties in the pH value”.

Line 56: Delete "O_2 is abundant in the atmosphere," this is an atmospheric chemistry journal.

Response:

Agree. In the revised manuscript, we will delete this sentence.

References

Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T., and Worsnop, D. R.: Mass accommodation and chemical reactions at gas-liquid interfaces, Chem. Rev., 106, 1323-1354, 10.1021/cr040366k, 2006.

Liu, Y. J., Zhu, T., Zhao, D. F., and Zhang, Z. F.: Investigation of the hygroscopic properties of Ca(NO3)(2) and internally mixed Ca(NO3)(2)/CaCO3 particles by micro-Raman spectrometry, Atmos. Chem. Phys., 8, 7205-7215, 2008.

Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.

Zhao, D., Song, X., Zhu, T., Zhang, Z., and Liu, Y.: Multiphase Reaction of SO2 with NO2 on CaCO3 Particles. 1. Oxidation of SO2 by NO2, Atmos. Chem. Phys. Discuss., 2017, 1-23, 10.5194/acp-2017-610, 2017.

Zhao, D. F., Zhu, T., Chen, Q., Liu, Y. J., and Zhang, Z. F.: Raman micro-spectrometry as a technique for investigating heterogeneous reactions on individual atmospheric particles, Sci. China Chem., 54, 154-160, 10.1007/s11426-010-4182-x, 2011.