Comments by Referees are in blue. Our replies are in black. Changes to the manuscript are highlighted in red both in here and in the revised manuscript.

Reply to Ref #1

This study reports room temperature uptake coefficients of chlorine nitrate (ClONO2) on TiO2 and SiO2 aerosol particles as well as on a macroscopic Pyrex surface. ClONO2 is implicated in the chlorine activation cycles sustaining stratospheric ozone loss and the formation of the polar ozone hole. This study is motivated by the proposals to use the injection of highly refractive nanomaterials, such as TiO2, into the stratosphere as a climate engineering measure to reduce solar radiation on the ground. Adding a substantial amount of TiO2 to the stratosphere is directly increasing the surface area for those heterogeneous processes normally occurring on polar stratospheric clouds or sulfuric acid particles of volcanic origin. ClONO2 hydrolysis is one of the key processes therein. Therefore, this study is addressing a highly relevant topic. The potential adverse (chemical) effects of solar radiation management schemes need careful attention. Apart from the laboratory measurement of the uptake coefficients, a global chemistry-climate model is used to assess the impact of TiO2 on stratospheric ozone in comparison to the sulfuric acid particle injection following the eruption of Pinatubo by tuning the TiO2 injection to have the same radiative properties as the Pinatubo sulfuric acid particles.

The results demonstrate uptake coefficients on TiO2 in the range of 1e-3 in the lower relative humidity range, which is significantly lower than hydrolysis on liquid sulfuric acid. For SiO2, uptake coefficients remained in the few 1e-4 range, about an order of magnitude larger than those observed on Pyrex, indicating the importance of representing the material of interest in the form most relevant for the atmosphere. The model work showed that injecting TiO2 into the stratosphere leads to two partially counteracting effects due to the altitude dependence of the efficiency of different species families involved in catalytic ozone loss: While the uptake of ClONO2 on TiO2 leads to less chlorine activation than would occur on sulfuric acid, the concomitantly smaller N2O5 uptake on TiO2 than on sulfuric acid results in lower ozone levels in the middle stratosphere. Therefore, within the constraints of a still not sufficiently established heterogeneous chemistry scheme, the effect of TiO2 on column ozone abundances remained similar to those of an equivalent sulfuric acid injection.

This study is well designed and performed and uses state of the art methods to address the kinetics of heterogeneous reactions. ClONO2 is an inherently difficult species to work with, and the efforts of the authors to synthesize, measure and calibrate it are appreciated. Only a few minor issues may remain as additional discussion topics with respect to the experimental part of the work. The model runs appear to be well designed, even though this reviewer is not familiar enough with modelling to judge the details. The manuscript is generally well written. A few comments below indicate where the structure could be improved.

Author reply: We would like to thank Ref #1 for his/her highly positive comments on our manuscript. All the comments have been properly addressed in our revised manuscript, as detailed below.

Specific comments

1. Introduction section: the authors should somewhere address the fact that TiO2 is a well-known photocatalyst, which may trigger radical production and chemical conversions, both oxidation and reduction. Are there estimates whether this could be relevant? Also, the photochemical activity is strongly size dependent and restricted to the size range used in this study. The authors should clarify whether the type of material studied here would be the one foreseen for the solar-radiation management purpose.

Author reply: This comment is very insightful. However, the effects of heterogeneous photochemical reactions (of TiO_2 and other potential SRM materials) on stratospheric chemistry have never been studied, and we are unfortunately unable to foresee a material for SRM. To make this clearer, the last sentence in the third paragraph of the introduction section has been expanded (page 4-5, line 87-89): "TiO_2 is an active photo catalyst (Shang et al., 2010; Chen et al., 2012; Romanias et al., 2012; Kebede et al., 2013; George et al., 2015) and the effects of its photochemical reactions on stratospheric chemistry, if injected into stratosphere for the purpose of climate engineering, are unknown. Therefore, its atmospheric heterogeneous photochemistry deserves further investigation."

2. section 4.1: since the measured uptake coefficient were rather close to the diffusion limit, the relevance of these values is rather limited. This section could therefore be condensed a bit. I suggest to add either the effective (uncorrected) uptake coefficients or the correction factor to table 1, so that the magnitude of correction becomes immediately apparent.

Author reply: We agree that the relevance of Section 4.1 is quite limited. Section 4.1 only contains two paragraphs and is difficult to be further shortened. We agree to include the effective uptake coefficients in Table 1. This has been done in the revised manuscript, and the table caption and related contents in Section 4.1 (page 17, line 386-387) have been updated accordingly.

3. page 17, lower paragraphs: while I agree that the local diffusion around the particles is not having an effect, I wonder whether the obviously strong radial gradients have an impact on the measured uptake coefficient. The effective first order wall loss rate coefficient is only acting on the average concentration.

Author reply: The referee is correct, and in fact this effect has been corrected. In the revised manuscript (page 18, line 409-411) we have added one sentence for explanation: "Axial and radical diffusion of $ClONO_2$ could lead to biases in its measured loss rates in a flow tube, and this effect, though very small (<10% in our work), has been corrected (Brown, 1978)."

4. page 20, top paragraph: it is not surprising that $ClONO_2$ hydrolysis behaves differently than N_2O_5 hydrolysis. However, from the discussion given here, it is not becoming apparent in what way the authors think the two mechanisms are operating such that $ClONO_2$ hydrolysis behaves as observed. Both processes

are likely initiated by OH groups, and both require adsorbed water. Is it maybe because for N_2O_5 two steps are required?

Author reply: Our measurements found that $\gamma(ClONO_2)$ is larger for TiO_2 but $\gamma(N_2O_5)$ is larger for SiO_2. We have realized our initial explanation is ambiguous. Therefore, in the revised manuscript we have changed the last sentence of this paragraph (page 21, line 483-486) to "This may indicate that a different mechanism controls N_2O_5 uptake by mineral surfaces. However, mechanistic explanations of the different heterogeneous reactivities of N_2O_5 and $ClONO_2$ on TiO_2 and SiO_2 surface at the molecular level cannot be derived from our data."

5. page 20, section 4.4 first paragraph: if Molina et al. have not done any control experiments in absence of HCl, I suggest to reduce this comparison to a minimum. It is rather trivial that the uptake on TiO2 in absence of HCl is different to that on alumina in presence of HCl. So there would be simply no data to compare with. In turn, the temperature dependence may indeed be important and should be carried into the modelling study as a big uncertainty.

Author reply: We agree with Ref #1 that it is expected that the presence of HCl will affect heterogeneous chemistry in the stratosphere. Nevertheless, we believe that it could be beneficial for a general audience to discuss the work carried out by Molina et al. in some details.

We also agree that the temperature dependence may cause large uncertainties. This is addressed together with next comment (point 6) raised by ref #1.

6. page 23, top paragraph: somewhere here the authors should address the sensitivity of the model runs to the temperature dependence of the uptake coefficient. I am not convinced that the studies cited for other species are giving a good indication for the potential T dependence for $ClONO_2$.

Author reply: We agree that our indication for potential temperature dependence is highly uncertain. In addition, sensitivity studies will be presented in a coming modeling paper. Therefore, in the revised manuscript we have rephrased the last sentence (page 24, line 567-571): "However, it is unclear whether temperature would have a significant effect on $\gamma(ClONO_2)$ for TiO_2 particles, and therefore our simulated impact of heterogeneous reaction of $ClONO_2$ with TiO_2 on stratospheric chemistry may have large uncertainties. The sensitivity of simulated stratospheric compositions to $\gamma(ClONO_2)$ for TiO_2 particles will be investigated in a following paper."

7. page 24, last part of discussion of modelling section: it is not clear to this reviewer what level of detail is included for the treatment of polar ozone, the occurrence and composition of PSCs etc. A few times, particularly strong effects at high latitudes are mentioned. It might be insightful to learn about the reasons for differences at high latitudes.

Author reply: As suggested, a description of modelled polar processes, and appropriate references, has been added to section 3 of the manuscript (page 14, line 320-324).

8. section 6: this section is not written as a conclusion. This is more a reiteration of the discussion and is partially repetitive. I suggest to integrate the important points to the previous sections and condense the rest into a real conclusion section. And since this rest contains quite a bit of statements and suggestions, I would entitle it as 'conclusions and outlook'.

Author reply: Indeed Section 6 includes some statements and suggestions, and as suggested, in the revised manuscript we have change its title to "Conclusions and outlook". We also agree that this section is partially repetitive. Nevertheless, we believe this information is appropriate in this section for those readers who may only briefly look at this study.

Technical comments

Page 2, abstract, line 20: revise sentence: 'Introduction of . . .would scatter solar radiation'; it is the particles that have an effect, not the introduction!

Page 7, line 160: . . .was then passed through. . .

Page 9, line 208: . . .served as a dry atmosphere. . .

Page 18, line 421: . . .The heterogeneous reaction . . .was studied. . .

Page 19, line 456:. . .adsorbed water on the SiO2 surface. . .

Page 22, line 527:. . . has a much smaller impact . . . than. . .(not 'reduced impact')

Page 23, line 558: In contrast, . . .

Author reply: We would like to thank Ref #1 for carefully reading our manuscript. All the typos have been corrected in the revised manuscript.