The comments from referee #1 are in blue, and our replies are in black. The major changes to the manuscripts are highlighted in red in both the manuscript and this reply.

The research carried out on the uptake of N2O5 on TiO2 was done very systematically and the manuscript is well written. The manuscript describes the determination of the uptake coefficient of N2O5 on TiO2 particles at room temperature for the first time. Since the refractive index of TiO2 is more than 60% greater than that of H2SO4 particles, main light scattering particles in the stratosphere, it requires much less amount to inject into the stratosphere to reduce the global warming. Unlike H2SO4, TiO2 would not presumably activate chlorine production to cause ozone-destructing chain reaction. Consequently, it would increase stratospheric ozone, thereby lowering photolysis rates in the troposphere and increases in N2O5 concentration.

I have only some minor comments:

Reply: We appreciate the very positive comments from referee #1, and would like to thank him/her for the recommendation of publishing our manuscript.

1. page 4424, para 1: How much TiO2 has to be injected into the stratosphere to have a perceptible impact?

Reply: The referee has raised a good question, though it is not easy to define “a perceptible effect”. The use of TiO_2 for SRM requires a factor of ~3 less in mass compared to sulfate. Since in this manuscript we always use the eruption of Mt. Pinatubo as a reference, at the end of this paragraph we have added a sentence in order to give an idea of the amount of TiO_2 needed: “i.e., only 10 Tg TiO_2 particles are needed (Pope et al., 2012)”.

2. What are other pathways for N2O5 loss on TiO2 than just hydrolysis? Is it possible to have NO2 produced as a result of the uptake? In such a situation, what would be the impact in terms of ozone depletion?

Reply: We believe that the uptake of N_2O_5 onto TiO_2 only leads to the formation of nitric acid and nitrate on the particles, according to previous studies on the heterogeneous reaction of N_2O_5 with mineral particles. To make it clearer, we have added one sentence to the last paragraph in page 4425: "Seisel *et al.* (2005) observed the formation of nitrate on mineral dust particles due to the uptake of N_2O_5 using diffuse reflectance FTIR, and Tang *et al.* (2012) further confirmed that the yield of nitrate is ~2 (as expected from R1) within the experimental uncertainty, and that the formation of NO_2 is negligible".

3. page 4430, lines 15-24: This assumption is fine on a relative scale. However, one N2O5 does not give one NO2 and one NO3. There is always some loss of NO3 to give NO2 + O2.

Reply: We do not quite agree with the referee. In fact this is a well-established method to measure N_2O_5. At the end of this paragraph we have added a sentence to explain it: "This scheme has been suggested as an absolute method to calibrate other N_2O_5 detection methods (e.g. CIMS) (Fahey et al., 1985), and is widely used to study the heterogeneous reactions of N_2O_5 with aerosol particles (e.g., Wagner et al., 2008)."

4. Page 4434, line 10- 25: It is good to see a detailed and rigorous of the diffusion correction. However, diffusion correction for small uptake coefficient values is negligible.

Reply: As the referee points out, the diffusion correction is negligible because of the small uptake coefficients determined in our study. We prefer to keep the detailed description of the rigorous correction method, because the new aerosol flow tube in the Cambridge lab is described here for the first time here.

Page 4438, line 13: "P25" should be "P2.5"

Reply: This is not a typo. It is the type of TiO_2, which we used for our study of "P25".

This paper is by no means a complete study as pointed out by authors regarding the photocatalytic activity of TiO2. However, it did a comprehensive experiment and discussion of the results on the uptake of N2O5 on TiO2 particles.

Reply: We appreciate the very positive comments from the referee. Indeed as he/she says, this is not a complete study regarding the potential chemistry of TiO_2 particles under stratospheric conditions. We have added two sentences in line 17 of page 4441 to the discussion, highlighting the importance of heterogeneous chlorine activation: "Heterogeneous chlorine activation is not included in the modeling work because of the lack of reliable kinetics data. The uptake of ClONO2 onto airborne mineral particles is under investigation in an ongoing study, and new laboratory data will be included in the model to assess the effect of heterogeneous chlorine activation on stratospheric O_3 in future work".

Page 4441, line 29 (last line): "feebacks" should be "feedbacks".

Reply: Thank you, the typo was corrected.

This manuscript should be accepted after addressing a few minor points.

Reply: We would like to thank the referee for his/her comments and support of publishing our manuscript.

References:

Fahey, D. W., Eubank, C. S., Hubler, G., and Fehsenfeld, F. C.: A Calibrated Source of N2O5, Atmos. Environ., 19, 1883-1890, 1985

Seisel, S., Borensen, C., Vogt, R., and Zellner, R.: Kinetics and mechanism of the uptake of N2O5 on mineral dust at 298 K, Atmos. Chem. Phys., 5, 3423-3432, 2005

Tang, M. J., Thieser, J., Schuster, G., and Crowley, J. N.: Kinetics and mechanism of the heterogeneous reaction of N2O5 with mineral dust particles, Phys. Chem. Chem. Phys., 14, 8551-8561, 2012

Wagner, C., Hanisch, F., Holmes, N., de Coninck, H., Schuster, G., and Crowley, J. N.: The interaction of N2O5 with mineral dust: aerosol flow tube and Knudsen reactor studies, Atmos. Chem. Phys., 8, 91-109, 2008.

The comments from the editor (also referee #2) are in blue, and our replies are in black. The major changes to the manuscripts are highlighted in red in both the manuscript and this reply.

Thank your for your contribution to ACP. Unfortunately one Referee did not submit a report in time, so I provide a quick review to substitute a report of one Referee.

The manuscript describes the uptake of N2O5 to TiO2 aerosol and the impact of this on stratospheric N2O5 and ozone budgets. Such studies are highly relevant and needed to understand the consequences of recently proposed approaches of solar-radiation management. The study is carefully done and analysed, conclusions are well justified and limitations are highlighted. Even though it is not a complete study, I accept this manuscript for publication in ACP after some minor changes.

Reply: We would like to thank the editor for his time spent on our manuscript, and his positive comments.

There are three main aspects that I ask you to discuss in more detail: * Could you give more details on the humidity and temperature conditions in the stratosphere for the altitude that shows highest TiO2 concentrations after injection. This would help the reader to relate your experimental study to the relevant environmental conditions. I feel that currently the relevance of the experimental settings is addressed rather late in the manuscript and the reader keeps wondering why you did experiments at RT and whether or not the RH are appropriate for the stratosphere.

Reply: It is a very good point. In the last paragraph of Page 4425 (ACPD) we have added a few sentences to explain it: "We note that in lower stratosphere the typical temperature and RH ranges are 200–220 K and <40 %, respectively (Dee et al., 2011). While our experimental work covers the RH range relevant for the stratosphere, it has been carried out at room temperature instead of ~200 K due to experimental difficulties."

* You nicely show and discuss the dependence of N2O5 uptake on relative humidity and conclude that the water at the TiO2 surface is relevant. Taken that temperature is lower in the stratosphere than at RT (where I assume the Goodman, 2001, data were derived); how would the water coverage look like at stratospheric temperatures; is that known?

Reply: The surface coverage of H_2O depends first on relative humidity (RH), and probably also temperature; however, data at low temperature is not available. At the end of section 3.2 we have added a few sentences to explain it: "The surface coverage of water is determined by RH, and is probably also affected by temperature. However, the RH-dependent water surface coverage has only been investigated at room temperature but not under lower stratospheric conditions (200-220 K)."

* What is the effect of N2O5 ↔ NO3 +NO2 equilibrium on your results. Removing N2O5 by uptake might lead to re-formation from NO3 and NO2. Did you by-pass the 100 ^{o}C reaction chamber occasionally to observe changes in NO2?

Reply: The NOx analyzer used in this work could not differentiate NO2 and N2O5, because they both (if the 100 °C reactor if bypassed) will be converted in the catalytic convertor to NO which is then measured by the chemiluminescence method. It is why in this work we use an indirect method to measure N2O5 by measurement of the NO change.

The effect of this equilibrium on the N2O5 uptake measurement has been discussed in details by Tang et al. (2012). In the revised version we briefly discuss this effect at the end of section 3.1: "The recombination of NO_2 with NO_3 (R4a) leads to the formation of additional N_2O_5, and the removal of NO_3 by the aerosol and wall surface causes further removal of N_2O_5 (R4b). Wagner et al. (2008) and Tang et al. (2010) simulated the effects of these reactions on N_2O_5 uptake measurement, and concluded that at room temperature the influence is negligible."

Further, I hope you'll find the following detailed comments helpful: P4424 l15ff: Reword: This implies a connection between low stratospheric ozone and decrease in surface temperature.

Reply: In the revised version we have revised it to "The eruption of Mt Pinatubo introduced an additional 30 Tg of aerosols into the stratosphere. This increased aerosol loading resulted in surface cooling and produced record low levels of stratospheric ozone (Dutton and Christy, 1992; McCormick et al., 1995)."

P4428, l20 ff: Could you include some more details about the experimental set-up such as concentration. What does "largely reduce NO2" mean exactly.

Reply: In L12-13, Page 4429 of the ACPD paper, we have changed the sentence to "This procedure was found to largely reduce the NO_2 impurity which was not completely oxidized by O_3 and thus also trapped in the cold finger at -76 ^{o}C during the N_2O_5 synthesis." At the end of section 2.1.4, we have added a sentence to give the N2O5 concentration used in our study: "The initial N_2O_5 mixing ratios used in in the flow tube were in the range of 1-2 ppmv."

P 4430 l10: Wagner described this synthesis first, didn't they? Could you add a reference?

Reply: This scheme was developed by Fahey et al. (1985), and our work largely followed that described by Wagner et al. (2009). At the end of this paragraph we have added a sentence to acknowledge both studies: "This scheme has been suggested as an absolute method to calibrate other N_2O_5 detection methods (e.g., CIMS) (Fahey et al., 1985) and is widely used to study the heterogeneous reactions of N_2O_5 with aerosol particles (e.g., Wagner et al., 2008)."

P4433 l9: "The difference of kw measured before and after introducing TiO2 aerosols in the AFT was insignificant, indicating that the N2O5 wall loss did not change significantly during the uptake experiment." How much did it change usually, could you specify.

Reply: The change is within the experimental uncertainties. We have specified it in the revised version: "was within the experimental uncertainty associated with k_w determination."

P4433 l15. It is not clear what "true loss rate" means in this context, could you specify?

Reply: We have modified it in the revised version: "The direct derivation of loss rates from exponential decays (e.g., Fig. 3) assumes the plug flow condition and no radical/axial diffusion. However, under laminar flow conditions the flow is non-plug and axial and radical diffusion also contribute to the apparent (or experimentally derived) loss of N_2O_5; therefore, the true loss rate is different from the apparent loss rate."

P4433 l 18+19: Change to Author (year)

Reply: We have changed it to "flow tube studies (e.g., Thornton et al., 2003)".

P 4433 l25: define gamma and gamma(eff) and gamma(exp)

Reply: In the ACPD paper we described the relation between γ and γ_{eff}. In the revised version we have added a sentence to define γ before we give the equation (2): "The rate of a heterogeneous reaction is usually described by the uptake coefficient, γ, which is equal to the probability that a gas molecule which collides with the surface is removed from the gas phase."

P4437l10: Why "Another"?

Reply: We have changed it to "The".

P4439l24 I don't understand this: ,"and this may be a result of an overestimate of surface area densities caused by extrapolation over the poles"

Reply: There are missing values in the observations used to construct the surface area density data set. Over the poles the missing values in the data set are filled by extrapolating the closest values. As with all extrapolations this produces an element of uncertainty, including spurious fluctuations. We have changed this sentence to "and this may be a result of overestimating surface area densities over the poles where have no observational data constraint."

P4440l10: "Whilst we acknowledge that there are limitations to these simulations, most notably the inclusion of only a single heterogeneous process on the TiO2, but also due to factors such as the omission of the TiO2 aerosols from the photolysis calculation, we believe the qualitative conclusions from them are valid." This sounds a little vague. Could you summarize why your believe this?

Reply: We have added a few sentences to explain further it: We base this on our understanding of the atmospheric response to the eruption of Mt. Pinatubo. Here the dominant factor on the global stratospheric chemistry was the increased heterogeneous chemistry, with factors such as changes in photolysis rates being secondary. However, further studies are required on effects on changes in photolysis before any definite conclusions can be reached.

P4441l15: At what concentration did Molina 1997 study the uptake? Are those atmospherically relevant?

Reply: We have expanded this sentence to include more details of Molina et al. (1997) in the revised version: One previous study (Molina et al., 1997) investigated the uptake of ClONO2 (1-10 $\times 10^{-7}$ Torr) onto aluminum oxide and Pyrex glass in the presence of HCl (1-10 $\times 10^{-6}$ Torr) at 210-220 K, and suggested that this process is very efficient, with an uptake coefficient of 0.02, which is >10 times larger than that onto stratospheric sulfuric acid aerosols.

P4442: What is QBC?

Reply: We have changed it to “Quasi-Biennial Oscillation”.

P4445, Caption fig 4: could you add experimental settings?

Reply: Figure 4 presents the uptake coefficients measured in this work, and experimental details were given in the initial ACPD paper. Therefore we think that the editor asked for some experimental details of Goodman et al. (2001). In the revised version we have changed “reported by Goodman et al. (2001)” to “measured by Transmission FT-IR spectroscopy (Goodman et al., 2001)”.

Section 3.1 and 3.2: What is the surface coverage of N2O5 and of H2O? How important is the thermal N2O5-NO2 equilibrium as source of uncertainties? Did you observe NO2 upon N2O5 uptake, or do your data suggest that N2O5 is completely taken up (as 2 HNO3) by the aerosol? Did this depend on humidity?

Reply: 1) Surface coverage of H_2O depends on RH, shown in Fig. 4 by citing the work of Goodman et al. (2001). N_2O_5 is converted to HNO_3 after uptake on the surface, so it may not have a surface coverage.

2) The effect of this equilibrium is addressed in a previous reply to your comment.

3) Unfortunately the detection used in this work does not have selectivity towards NO_2. However, Tang et al. (2012) confirmed that the formation of NO_2 in the N_2O_5 uptake is negligible. In the last paragraph of Page 4425 (ACPD), we have added a few sentences to make this clear: "Seisel et al. (2005) observed the formation of nitrate on mineral dust particles due to the uptake of N_2O_5 using diffuse reflectance FTIR, and Tang et al. (2012) further confirmed that the yield of nitrate is ~2 (as expected from R1) within the experimental uncertainty, and that the formation of NO_2 is negligible."

Introduction or Discussion: Are there other important loss processes in the stratosphere, i.e. photolysis that might be changed by TiO2 (and the induced changes on radiation). Could you elaborate on this?

Reply: We have modified Line 22-25, Page 4441 to discuss further heterogeneous photochemical reactions which might have some importance: "For example, the uptake of NO_2 on TiO_2 particles is enhanced under irradiation (Ndour et al., 2008; El Zein and Bedjanian, 2012), leading to the formation of HONO, the photolysis of which produces NO and OH and may perturb the stratospheric NOx and HOx cycles. Heterogeneous chemical oxidation of SO_2 could enhance the formation of sulfate coating on mineral particles (Shang et al., 2010)."

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El Zein, A., and Bedjanian, Y.: Interaction of NO2 with TiO2 surface under UV irradiation: measurements of the uptake coefficient, Atmos. Chem. Phys., 12, 1013-1020, 10.5194/acp-12-1013-2012, 2012.

Fahey, D. W., Eubank, C. S., Hubler, G., and Fehsenfeld, F. C.: A Calibrated Source of N2O5, Atmos. Environ., 19, 1883-1890, 1985.

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