Dear anonymous reviewers,

Thank you very much for your comments on our manuscript [acp-2014-255]. Your comments and suggestions are valuable and very helpful for improving our manuscript. Based on your comments and suggestions, we carefully revised the manuscript, and the point-by-point responses to your comments and suggestions are listed below.

Thank you once again for your time and consideration.

Responds to the comments:

Note: All the revisions are based on the previously submitted manuscript in word format which corresponds to the ACPD. For the modified portions, we provide the page and line numbers of the manuscript in word format before modification. At the same time, we also indicate the corresponding page and line numbers in ACPD in the brackets when revision needs to be made.

Anonymous Referee #1

This laboratory study demonstrates the positive effect that nitrate has on the heterogeneous oxidation of sulfur dioxide on hematite. The resulting acidification of the surface and formation of sulfate is monitored by DRIFTS, while release of nitrous acid and nitrous oxide has been observed by FTIR. Sulfur (IV) oxidation on mineral dust has been the target of many studies in the past, but the novel aspect here is that the authors uncover the linked redox cycles of iron, nitrogen and sulfur, where iron (III) acts as an oxidant for sulfur dioxide and iron (II) as a reductant for nitrate.

By themselves, the experiments seem to be well performed and analyzed; however, some concerns remain with respect to the way samples were prepared and exposed in the DRIFTS experiments. These will not affect the general conclusion about the convoluted redox chemistry but will affect the extrapolation to atmospheric conditions.

While the samples are prepared by equilibrating the hematite powder with the nitrate salt at 68% relative humidity, once the samples are introduced to the DRIFTS cell, they are not exposed to humidity anymore (correct?) and will therefore dry out during the actual sulfur oxidation experiments. Therefore, significant changes in the physical properties are induced (over what time scale?), which likely suppress the efficiency of the redox cycles, which would require some aqueous phase to allow exchange of ions by diffusion. This aspect needs to be considered in the experimental and results/discussion sections.

We thank you for your valuable comments. For the way samples were prepared: In our manuscript, we described the preparation method of the FN series. In fact, in order to compare the reactivity of samples, all of the samples were treated by equilibrating the powder at 68% relative humidity for the same time (48 h) before further use. Therefore, on page 6, line 129 (page 11582, line 2 in ACPD), we delete "at least" from "…for at least 48 h… ".

In our study, the nitrate-hematite mixtures and pure nitrate are still loose fine powders after they are equilibrated at 68% RH for 48 h. For example, for FN-24 sample, we give its digital photo after equilibration for 48 h (see Fig. R1). As can be seen from Fig. R1, there may be some water molecule layers resisting on humid sample surfaces, but the nitrate and hematite are not immersed in a solution after the equilibration in our experiments. This is the reason why we use "humid" instead of "wet".

For the way samples were exposed in the DRIFTS experiments:

In the DRIFTS experiments, the used gaseous oxygen, argon and SO_2 were dried. That is, once the samples are introduced to the DRIFTS cell, they are not exposed to humidity anymore. Just as you think, the introduction of the dried gases into the DRIFTS cell will cause a loss of surface adsorbed water. During purge process, we found that the loss of water is almost stopped after about 40 min, and on the whole, the loss of water is low. The loss of surface adsorbed water (around 1640 cm^{-1}) is not easy to be observed after the introduction of the gaseous reactant SO_2 (using a background spectrum measured on the powder sample which was purged with argon for 1 h), which indicates less water loss. These results may be attributed to the presence of nitrate. That is, the water-solvated nitrate bound water molecules on the particle surface due to its hygroscopic properties, and the solvated nitrate may become a water reservoir for reaction. Weak water loss will favor the redox cycles (The anonymous referee #2 also concerns about the loss of water during the experiments. In the answer to the question 8 in general comments of anonymous referee #2, we give some experimental results and discuss the loss of surface adsorbed water during the purge process and the actual sulfur oxidation experiments. Please refer to the answer.).

In addition, this is a good idea. We will further design and conduct such experiments in which the relative humidity is controlled at different values during the whole experiment.

The manuscript is unnecessary long, even though it is in general reasonably well written. Most of the discussions are too detailed and repetitive and distract from the main line of the paper. This could be solved for instance by placing the detailed spectral IR assignments into a supporting online part and only integrate the result of that into the main paper. Several other sections could be shortened in the same way, such that an overall much more concise paper with the main aspects would result.

We accept this suggestion and made some substantial revisions according to your detailed comments.

Detailed comments:

(1) P4, top paragraph: To what degree has the work by Harris et al. (2013) on the role of transition metals in cloud oxidation resolved the issue of missing sulfate sources?

Reference

Harris, E., Sinha, B. r., van Pinxteren, D., Tilgner, A., Fomba, K.W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., and Herrmann, H.: Enhanced Role of Transition Metal Ion Catalysis During In-Cloud Oxidation of SO_2, Science, 340, 727-730, 2013.

We read the paper carefully. In the paper, Harris et al. found that sulfur dioxide oxidation catalyzed by natural transition metal ions is the dominant in-cloud oxidation pathway, and including this pathway in models will improve agreement between modeled and observed SO_2 (or sulfate) concentrations. Maybe this pathway is significant in clouds, and taking this into account will lead to large changes in estimates of the magnitude and spatial distribution of aerosol forcing, but this pathway may be still insufficient to resolve the model discrepancies with surface SO_2 and sulfate observations. One the one hand, this is because that there are large uncertainties in atmospheric dissolved transition metal ions concentrations. On the other hand, this is because that the atmospheric heterogeneous reactions of SO_2 on aerosol surfaces still have large uncertainties.

We cited this paper in the revised manuscript, and appropriate revisions have been made as follows:

On page 3, line 57-59 (page 11579, line 11-13), "…, and the two pathways including gaseous oxidation by OH radical and aqueous oxidation in cloud and fog droplets by ozone and hydrogen peroxide are insufficient to bridge the gap between field and modeling studies (Luria and Sievering, 1991). Including in-cloud oxidation catalyzed by natural transition metal ions in models will improve agreement between models and observations (Harris et al., 2013). These imply that…".

(2) P5, lower paragraph: this should be shortened substantially. The involvement of HNO_3 and HONO is not introduced before and thus should not appear here.

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

On page 5, line 105-110 (page 11581, line 3-8), the original part is revised to "The results reveal a potential pathway of sulfate formation in the troposphere and the significant contribution of particulate nitrate for the conversion of SO_2 and the enhanced formation of sulfate in the atmosphere.".

(3) Line 130: 'desiccator' is probably not the right word, since the vessel has been used to expose the sample to high humidity and not to dry it. This word is causing

confusion here.

The reason we used this word is mainly that we referred to some published papers such as the following:

Hong, T. D., Edgington, S., Ellis, R. H., de Muro, M. A., and Moore, D.: Saturated salt solutions for humidity control and the survival of dry powder and oil formulations of Beauveria bassiana conidia, J. Invertebr. Pathol., 89, 136–143, 2005.

Kuu, W. Y., Chilamkurti, R., and Chen, C.: Effect of relative humidity and temperature on moisture sorption and stability of sodium bicarbonate powder, Int. J. Pharm., 166,167–175, 1998.

Sandoval, A. J. and Barreiro, J. A.: Water sorption isotherms of non-fermented cocoa beans (Theobroma cacao), J. Food Eng., 51, 119-123, 2002.

The main and secondary chambers of a desiccator are usually separated by a removable platform. The secondary chamber is used to place the selected saturated salt solution to produce the desired relative humidity. The sample was treated in the main chamber by equilibrating the powder at the desired relative humidity. This method of sample treatment is so-called “static desiccator method” or “static desiccator technique”. Therefore, we used this word in the manuscript.

(4) Line 132: ‘saturation’ should be replaced by ‘equilibration’

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

On page 6, line 131 (page 11582, line 3), “saturation” is replaced by “equilibration”.

(5) Section 2.2: Here, it should be explicitly stated and explained what happens with the water, once the sample is in the DRIFTS cell.

We accept this suggestion, and corresponding revision has been made in the revised manuscript (Please refer to the answers to your question in general comments and the question 8 in general comments of anonymous referee #2. There, we discuss the loss of surface adsorbed water during the purge process and the actual sulfur oxidation experiments.):

On page 7, line 145 (page 11582, line 18), the content "In addition, it should be pointed out that weak surface water loss will be observed during the purge process, but the loss of water is almost stopped after about 40 min. Furthermore, less water loss is also observed after the introduction of the reactive gases. These imply that some water molecules are kept in the sample due to the presence of hygroscopic salt ($NaNO_3$)." is added.

(6) Section 2.4: Again, the final amount of water in the bottle after introducing the gases should be estimated to get an idea of the water activity within the sample.

From the point of view of water loss, the difference between this experiment and the DRIFTS experiment mainly lies in the former did not continuously load the reactive gases. That is, the bottle was purged with a mixture of dried Ar and O_2 (100 mL/min) for 1 h, after which the inlet and the outlet of the bottle were closed. Considering that less water loss is observed after the introduction of the reactive gases in the DRIFTS experiment, the final amount of water in the bottle after introducing gases should be close to that in the same sample in the DRIFTS cell.

Corresponding revision has been made in the revised manuscript:

Page 9, line 184 (page 11584, line 6): The content "After the above treatments, the final amount of water in the bottle should be close to that in the same sample in the DRIFTS cell." is added.

(7) Line 216: The preparation of the pure nitrate samples is not described in the experimental section. At high humidity it deliquescing and will form a solution?

In the experimental section, we add the following content in the revised manuscript:

Page 6, line 130-131 (page 11582, line 2-3), the sentence "The humid samples were still loose fine powders after the equilibration, …" is revised to "The humid samples including the hematite-nitrate mixtures, pure hematite and nitrate were still loose fine powders after the equilibration, …”.

Lee and Hsu (2000) observed that the water uptake by $NaNO_3$ particles was a continuous process between 25% and 89% RH. Gysel et al. (2002) found that $NaNO_3$ particles did not exhibit a deliquescence phenomenon using a tandem differential mobility analyzer. Gibson et al. (2006) observed that the diameter of $NaNO_3$ particles increased continuously from 100 nm at 10% RH to 158 nm at 83% RH using a multianalysis aerosol reactor system. Hoffman et al. (2004) also did not observe the deliquescence point of $NaNO_3$ particles by using several approaches. However, some researchers observed the deliquescence point of $NaNO_3$ particles. For example, Tang and Munkelwitz (1994) observed the deliquescence point of $NaNO_3$ particles at 74.5% RH at 25 ℃ using a single-particle levitation technique. Liu et al. (2008) observed a very sharp deliquescence transition at 71%-73% RH for $NaNO_3$ particles using microscopic Fourier transform infrared spectroscopy. Therefore, considering that the relative humidity used in our study is 68%, the deliquescence phenomenon should not be observed.

(8) P12/13: Also this part discussing the pure hematite case should be exported to the supporting online material. This is known from previous studies and serves more as a reference for the other experiments.

We accept this suggestion, and corresponding revisions have been made in the revised manuscript:

(1) The part on page 12-13, line 263-272 (page 11587, line 8-17) is exported to the supporting online material, and we put it together with Fig. S4.

(2) The part on page 13, line 272-284 (page 11587, line 17-29) is also exported to the supporting online material (Please see Section S6 in the Supplement). Correspondingly, on page 14, line 312 (page 11588, line 28), “see Section S6 in the Supplement” is added in the revised manuscript.

(9) P13: the discussion of FN samples in terms of adsorption configurations should be cautioned, since the system here is likely an amorphous nitrate film in contact with

hematite. What is the average thickness of the film if the nitrate is evenly distributed over the particles?

We once performed X-ray diffraction analyses of pure hematite, humid FN-24 and FN-48 (Fig. R2). The results are shown in the following figure. The crystalline peaks at 29.65 °, 31.9 °, 39.0 ° and 47.9 ° can be identified as the characteristic reflections of $NaNO_3$. No amorphous sodium nitrate was present because there was no broad amorphous peak in the 20 °- 40 ° range.

In addition, for the average thickness of the film, we are very sorry that we didn't focus on it during we performed SEM characterization, and we are unable to provide this data.

(10) Line 364: The surface complexes of N_2O_4 likely only exist at relatively high NO_2/N_2O_4 concentrations in the gas phase. Since the surface concentrations are low here, wouldn't N_2O_4 immediately decay into NO_2 and desorb under the conditions of the present experiments?

In the White cell-FTIR experiments, we did not find gas phase NO_2 and N_2O_4. We also analyzed the gas phase species in the White Cell reactor by using SPME-GC-MS technique, and no gaseous NO_2 and N_2O_4 is observed. Hence, we think that N_2O_4 can't immediately decay into NO_2 and desorb under the conditions of the present experiments. The reason may be as follows. On the one hand, a very small amount of N_2O_4 is formed on particle surface, the formed N_2O_4 may be captured by surface sulfite to initiate its secondary reaction, in addition to the interactions with HNO_3, HNO_3-H_2O complexes and H_2O. On the other hand, the concentration of the formed N_2O_4 is very low, even if the N_2O_4 is completely decomposed into NO_2 and the NO_2 desorbs from the surface into the gas phase, the concentration of the gas phase NO_2 is also low, which may make gaseous N_2O_4 and NO_2 be present at concentrations below detection limits.

(11) Line 464: what was the estimated partial pressure of HONO? Related to that, line 474: the self-reaction of HONO is probably not relevant at these HONO pressures?

We are very sorry that we haven't measured the partial pressure of HONO. We estimated that the partial pressure of HONO was very low because the absorption peaks of HONO were very weak. Therefore, as you point out, the self-reaction of HONO is probably not relevant at such low HONO pressures. Appropriate revision has been made in the revised manuscript:

Page 22, line 480 (page 11595, line 5-6): "Maybe gaseous NO and NO_2 are present at concentrations below detection limits." is replaced by "It is possible that gaseous NO and NO_2 are present at concentrations below detection limits. But on the other hand, the weak absorption peaks of HONO may suggest the very low HONO partial pressure, and hence the self-reaction of HONO is probably not relevant at such a low HONO pressure.".

(12) Page 25: The suggestion of the formation of N_2O as a product of secondary HONO chemistry is likely correct. However, in terms of atmospheric implications, the high surface to volume ratio of the experiments leads to relatively more N_2O than in the atmosphere. There, the lifetime of HONO is probably limited by photolysis. This should be discussed in the atmospheric implications section.

We accept this suggestion:

Page 25, line 546-549 (page 11597, line 15-18), this part has been revised into "The result may help to explain why the sources of N_2O exceed the estimated sinks in the atmosphere and the observed increase in atmospheric N_2O. However, it should be pointed out that the high surface to volume ratio of the experiments may lead to relatively more N_2O than in the atmosphere. Meanwhile the lifetime of HONO in the atmosphere is probably limited by photolysis. The relative importance of this source needs further study.".

(13) Page 28/29: in the discussion of the mechanism, the authors should come back to the fate of water during the experiments and the relevance of the fact of 'drying out' on the mechanism interpretation.

We accept this suggestion. Based on the above discussion, appropriate revision has been made in the revised manuscript:

Page 28, line 632 (page 11600, line 19): “and leads to weak water loss during the purge and subsequent reaction processes.” is added in the revised manuscript.

References

Gibson, E. R., Hudson, P. K., and Grassian, V. H.: Physicochemical properties of nitrate aerosols: Implications for the atmosphere. J. Phys. Chem. A, 110, 11785-11799, 2006.

Gysel, M., Weingartner, E., and Baltensperger, U.: Hygroscopicity of aerosol particles at low temperatures. 2. Theoretical and experimental hygroscopic properties of laboratory generated aerosols, Environ. Sci. Technol., 36, 63-68, 2002.

Hoffman, R. C., Laskin, A., and Finlayson-Pitts, B. J.: Sodium nitrate particles: physical and chemical properties during hydration and dehydration, and implications for aged sea salt aerosols, J. Aerosol Sci., 35, 869-887, 2004.

Lee, C. T. and Hsu, W. C.: The measurement of liquid water mass associated with collected hygroscopic particles, J. Aerosol Sci., 31, 189-197, 2000.

Liu, Y., Yang, Z., Desyaterik, Y., Gassman, P. L., Wang, H., and Laskin, A.: Hygroscopic behavior of substrate-deposited particles studied by micro-FT-IR spectroscopy and complementary methods of particle analysis, Anal. Chem., 80, 633-642, 2008.

Tang, I. N. and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance, J. Geophys. Res., 99, 18801-18808, 1994.

Anonymous Referee #2

This paper investigates the effect of nitrate on the heterogeneous conversion of SO_2 with hematite and hematite-nitrate mixtures using an in situ diffuse reflectance infrared Fourier transform spectroscopy and a long-path FTIR cell. They found that the presence of nitrate can enhance SO_2 oxidation to sulfate on hematite surface. The nitrate itself can convert into surface adsorbed HNO_3 and N_2O_4 as well as gas phase N_2O and HONO. The findings reveal a new SO_2 oxidation pathway as well as a potential source of N_2O and HONO in the atmosphere. The experimental methodology is sound. Equally sound is their interaction with the literature. The main issue of this paper is in the writing. There are many poorly worded sentences and grammatical errors. The poor writing lowers the paper quality and sometimes leads to confusion. Still, I would support publication of the manuscript after the details below have been addressed.

We are very sorry for the incorrect writing. Thank you very much for your suggestions. Based on your suggestions, we have revised the whole manuscript carefully and tried to avoid poorly worded sentences and grammatical errors.

General comments:

1) Page 11586, line 9-16. A figure showing band areas at 1260, 1158, 1056 and 1000 cm^{-1} with time should be added to the supplemental information.

According to your suggestion, a figure showing band areas at 1261, 1222 and 1158 cm^{-1} with time has been added to the supplemental information (please see Section S3, Fig. S4).

It should be pointed out that the figure has not shown the band areas at 1056 and 1000 cm^{-1} because the two bands have a very small change in band area with time.

In addition, as you known, peak fitting can produce bias, and hence the fitting band at 1222 cm^{-1} corresponds to the band at 1219 cm^{-1} in Fig. 1.

Corresponding revisions have been made in the revised manuscript:

Page 11, line 241 (page 11586, line 14). “(see Fig. S4 in the Supplement)” is added;

Page 15, line 324 (page 11589, line 12). “Fig. S4” is replaced by “Fig. S5 in the Supplement”;

Page 26, line 572 (page 11598, line 13). “Fig. S5” is replaced by “Fig. S6 in the Supplement”.

2) Page 11590, Figure 3. The authors did not discuss two adsorption bands peaked at 2887 and 1732 cm^{-1}, respectively. What species the two bands can be attributed to?

(1) A summary of the main peaks of adsorbed N_2O_4 reported in some earlier studies is given in Table R1.

Table R1. A summary of the main peaks of adsorbed N_2O_4 reported in earlier studies.

No.	Reference	Surface	Adsorbed N_2O_4 (cm^{-1})
(1)	Ma et al., J. Phys. Chem. A 2008, 112, 6630.	γ-Al_2O_3	1733 $\upsilon_a(NO_2)$
(2)	Goodman et al., J. Phys. Chem. A 1999, 103, 7217.	hydrated Silica	1744 broad peak
(3)	Barney et al., J. Phys. Chem. A 2000, 104,171.	porous glass	1740 broad peak
(4)	Wang and Koel, J. Phys. Chem. A 1998, 102, 8573.	Au(111)	1760 $\upsilon_a(NO_2)$, 1735 $\upsilon_a(NO_2)$
(5)	Koch et al., J. Phys. Chem. 1995, 99, 8362.	gold foil	1761 $\upsilon_a(NO_2)$ 1734 $\upsilon_a(NO_2)$
(6)	Mochida et al., J. Phys. Chem. A 2000, 104, 9705.	porous glass	1750 broad peak
(7)	Liu et al., Phys. Chem. Chem. Phys., 2012, 14, 1668.	mineral oxides	1749 broad peak
(8)	Finlayson-Pitts et al., Phys. Chem. Chem. Phys., 2003, 5, 223.	glass	1740 broad peak
(9)	Givan, A.; Loewenschuss, A. J. Chem. Phys. 1989, 90, 6135.	copper or gold coated copper plate	1750 $\upsilon_a(NO_2)$, 1728 $\upsilon_a(NO_2)$

Based on Table R1, the band at 1732 cm^{-1} in our study should be due to adsorbed N_2O_4. Therefore, some revisions have been made in the revised manuscript:

Page 16-17, line 358-368 (page 11590-11591, line 21-3). We have revised this part as follows:

"Two weak shoulder peaks at 1746 and 1732 cm^{-1} are seen to grow as the surface is exposed to SO_2. These two peaks should be attributed to the asymmetric $\upsilon_a(NO_2)$ stretch of N_2O_4 adsorbed on the surface, indicating the formation of adsorbed N_2O_4 (Goodman et al., 1999; Finlayson-Pitts et al., 2003). These peaks overlap with those of adsorbed HNO_3 and increase in intensity with the amount of adsorbed nitric acid on the surface. As previously reported, N_2O_4 can interact with HNO_3 and/or HNO_3-H_2O water complexes on particle surface through hydrogen bonds, in addition to the interactions with H_2O (Finlayson-Pitts et al., 2003). This further indicates that the formed N_2O_4 may be held on particle surface with nitric acid and H_2O present. This is consistent with the fact that no gas phase N_2O_4 was detected in White cell-FTIR experiments as discussed later."

(2) The OH stretching region is complicated. In previous studies, the OH stretching region often showed a broad absorption band extending from 3700 to 2700 cm^{-1}, and sometimes from 3700 to 2000 cm^{-1}(Goodman, et al., 1999; Börensen et al., 2000; Ramazan et al., 2006; Finlayson-Pitts et al., 2003.). In these studies, this broad peak is primarily associated with O-H vibration of hydrogen-bonded OH groups of acid such as HNO_3.

In our paper, we just marked some peaks including 2887 cm^{-1} and some other range. Considering that the broad absorption peak extending from 3500 to 2520 cm^{-1} increases in intensity slowly with the increase of reaction time in our study, we extend the range of the broad absorption peak, and appropriate revisions have been made in the revised manuscript:

Page 17, line 381 (page 11591, line 16-17), "extending from 2900 to 3500 cm^{-1}" is replaced by "extending from 3500 to 2520 cm^{-1}".

Page 18, line 385 (page 11591, line 20), "Goodman, et al., 1999;" is inserted.

Page 50 (page 11616), in Fig. 3, the peak at 2887 cm^{-1} is no longer marked, and the O-H vibration range has been adjusted.

For Supporting Information:

In Fig. S5, the marked O-H vibration range has been adjusted.

3) Page 11592, section 3.2. The authors calculated sulfate formation rates assuming the formation rates kept constant 'at the initial stages' for all samples. The authors provided a reference to support the assumption (Wu et al., 2011). It is not clear how long the DRIFTS experiments last. Is it 4 hours as stated in the caption of Fig. 4? Please clarify it in the text. Since surface active sites are limited, I expected that sulfate would reach a plateau if DRIFTS experiments last long enough. The authors should verify the assumption using DRIFTS data. A plot showing integrated areas of

sulfate with time would be useful.

We are very sorry that we did not describe clearly. In the captions of Figure 4 and Figure 9, we only paid attention to describe the experimental conditions, and neglected the statement of the "at the initial stage". In fact, in integrated areas of sulfate/time plot, we used the slope of the fitting linear portion within 2 h to determine sulfate formation rates. In most previous studies, the time used to calculate the initial formation rate is often not clear, and these studies only tell us that no saturation effects are expected or the slope of the linear portion in integrated areas of sulfate/time plot is used. Hence we chose the experimental data within 2 h. As can be seen from Fig.R3, no saturation effects are observed within 2 h. However, based on your comment, we read the paper by Wu et al. again, we find that our selected initial stage seemed to be too long. In addition, in the plot of integrated areas of sulfate with time, the initial region stated by Wu et al. seems to be different from ours.

In order to obtain the initial stage as short as possible, in Fig. R3, we select different reaction times to calculate the slopes. The results are shown in Table R2.

Table R2. Slopes obtained using different reaction times as initial stages.

Reaction time	120 min	100 min	80 min	60 min	40 min
slope	0.1731	0.1773	0.1788	0.1758	0.1658
R^2	0.997	0.997	0.995	0.991	0.975

From the linear correlation coefficient in the Table R2, we find that the data points still present good linear relationship within 60 min. Therefore, in the revised manuscript, we choose 60 min as initial stage for the related calculation again. Appropriate revisions have been made in the revised manuscript:

Page 19, line 408-411 (page 11592, line 17-20), this part has been revised into "The number of sulfate ions formed at the initial stage of reaction is generally considered to be small relative to the number of reactive surface sites, and thus the latter at initial stage can be assumed to be constant (Börensen, et al., 2000)."

Page 19, line 414 (page 11592, line 23), the content "and hence the experiments with different SO_2 concentrations were performed." has been revised into "For this purpose, the experiments with different SO_2 concentrations were performed, and the sulfate formation rate d[SO_4^{2-}]/dt was obtained from the slope of the initial linear portion (0-60 min) in the curve of sulfate formation as a function of time. No saturation effects on sulfate formation were observed.".

Your suggestion enhances our understanding of the sulfate formation rate calculations. Thank you for this good suggestion again.

4) Upper and lower limits of uptake coefficients can be calculated using the geometric area of the sample holder (assuming SO_2 only reaches the surface) and the BET surface area of the sample (assuming SO_2 can diffuse into the entire sample), respectively. Uptake coefficients can also be obtained using the white cell-FTIR data. Comparison of uptake coefficients obtained from two different methods would be insightful.

According to your suggestion and the previous advice of the anonymous referee #3 (before publication in ACPD), we calculate the sulfate formation rates (initial stage: 0-60 min) and the two kinds of uptake coefficients of SO_2 on hematite and the hematite-nitrate mixtures. The results are shown in Table R3 (i.e. Table 2 in the revised manuscript), and original Fig.4 is replaced by Table 2 in the revised manuscript.

Table R3. Sulfate formation rates and uptake coefficients for heterogeneous reactions of SO_2 on hematite and the hematite-nitrate mixtures at 298 K.

$NaNO_3$ (%)	A_{BET} (m^2/g)	Sulfate formation rate (ions s^{-1}) ($\times 10^{15}$)	$A_{geometric}$ (m^2) ($\times 10^5$)	γ_{BET} ($\times 10^7$)	$\gamma_{geometric}$ ($\times 10^3$)
0	12.1	1.28±0.07	7.85	5.58±0.29	2.58±0.14
2	11.8	1.48±0.15	7.85	6.60±0.69	2.98±0.31
4	11.7	2.01±0.12	7.85	9.04±0.56	4.04±0.25
6	11.5	3.62±0.18	7.85	16.6±0.81	7.29±0.35
12	10.9	4.93±0.29	7.85	23.8±0.14	9.93±0.58
24	9.1	7.11±1.34	7.85	41.2±0.78	14.3±2.69
48	5.2	4.39±0.39	7.85	44.5±0.39	8.84±0.78
60	4.0	1.62±0.25	7.85	21.3±0.32	3.25±0.49

72	2.8	0.59 ±0.15	7.85	11.2 ±0.29	1.19 ±0.31
90	1.3	0.15 ±0.03	7.85	6.10 ±1.05	0.30 ±0.05
100		0		0	0

Corresponding revisions have been made in the revised manuscript:

(1) The number of figures is adjusted:

Page 20, line 441 (page 11593, line 23): “Fig. 5” is replaced by “Fig. 4”.

Page 21, line 461 (page 11594, line 14): “Fig. 6” is replaced by “Figure 5”.

Page 21, line 463 (page 11594, line 16): “Fig. 6e” is replaced by “Fig. 5e”.

Page 21, line 463 (page 11594, line 17): “Fig. 6c” is replaced by “Fig. 5c”.

Page 21, line 464 (page 11594, line 17): “Fig. 6d” is replaced by “Fig. 5d”.

Page 21, line 464 (page 11594, line 17): “Fig. 6” is replaced by “Fig. 5”.

Page 21, line 466 (page 11594, line 20): “Fig. 6d” is replaced by “Fig. 5d”.

Page 21, line 467 (page 11594, line 20): “Fig. 6e” is replaced by “Fig. 5e”.

Page 24, line 529 (page 11596, line 26): “Fig. 6” is replaced by “Fig. 5”.

Page 24, line 533 (page 11597, line 1): “Fig. 6f” is replaced by “Fig. 5f”.

Page 25, line 555 (page 11597, line 24): “Figure 7” is replaced by “Figure 6”.

Page 27, line 587 (page 11599, line 1): “Figure 8” is replaced by “Figure 7”.

Page 27, line 588 (page 11599, line 2): “Fig. 8a, 8c” is replaced by “Fig. 7a and c”.

Page 27, line 588 (page 11599, line 2-3): “Fig. 8b, 8d” is replaced by “Fig. 7b and d”.

Page 27, line 593-594 (page 11599, line 8): “Fig. 8e” is replaced by “Fig. 7e”.

Page 28, line 613 (page 11599, line 27): “Fig. 9” is replaced by “Fig. 8”.

Page 33, line 734 (page 11604, line 18): “Fig. 10” is replaced by “Fig. 9”.

Figure caption:

Page 51 (page 11617), Fig. 4 is removed.

Page 52, line 1062 (page 11618): “Fig. 5” is replaced by “Fig. 4”.

Page 53, line 1077 (page 11619): “Fig. 6” is replaced by “Fig. 5”.

Page 54, line 1092 (page 11620): “Fig. 7” is replaced by “Fig. 6”.

Page 55, line 1112 (page 11621): “Fig. 8” is replaced by “Fig. 7”.

Page 56, line 1121 (page 11622): “Fig. 9” is replaced by “Fig. 8”.

Page 57, line 1138 (page 11623): “Fig. 10” is replaced by “Fig. 9”.

(2) Page 18, line 392 (page 11592, line 1-2), the subtitle has been revised into "3.2 Effect of nitrate on the rate of sulfate formation and uptake coefficient for SO_2 on hematite-nitrate mixture at 298 K".

(3) Page 19-20, line 421-432 (page 11593, line 3-14), based on the Table 2, appropriate revisions have been made in the revised manuscript, including the introduction of the calculation method of uptake coefficient, the calculated results and corresponding discussions. Please see the corresponding contents in the revised manuscript.

(4) Page 2, line 35 (page 11578, line 16-17) in Abstract, and Page 34, line 745 (page 11605, line 1) in Conclusion: the content "The sample containing 48% nitrate presents the highest BET uptake coefficient, and the value is about 8 times higher than that of pure hematite." is added.

(5) Page 2, line 30 (page 11578, line 12), the "small amounts of" is replaced by "low to moderate amounts of". Same applied to page 36, line 789 (page 11606, line 17);

Page 20, line 432 (page 11593, line 14-15), "a small amount of" is replaced by "a low to moderate amount of". Same applied to Page 34, line 742-743 (page 11604, line 25).

(6) Page 2, line 34 (page 11578, line 16), and page 34, line 745 (page 11605, line 1): Base on the recalculated results, the "about 5 times" is replaced by "about 5.5 times".

(7) Page 2, line 34 (page 11578, line 16), "average sulfate formation rate" is replaced by "uptake coefficient calculated by geometric surface area". Same applied to page 34, line 744-745 (page 11604-11605, line 27-1).

In addition, we also use the White-cell experimental data to calculate apparent rate constants of the heterogeneous reactions of SO_2 on different samples (deducting blank value obtained from blank experiment). For example, for a first order reaction, the apparent rate constants were determined to be 2.50×10^{-3} (r=0.93) and 6.40×10^{-3} (r=0.99) for uptake on pure hematite and FN-24, respectively. The former is close to that previously reported by Zhang et al. (Zhang, et al., 2006). The corresponding uptake coefficients calculated using BET surface areas were 1.47×10^{-7} and 5.02×10^{-7} for uptake on pure hematite and FN-24, respectively. The two values are slightly lower than those calculated by DRIFTS data respectively (approximately, both are at the same level). However, the reactivity trend of different hematite-nitrate mixtures is consistent with that observed in DRIFTS experiments. Gas diffusion limitation, reactor wall adsorption and desorption of reactive gases and some other factors may be responsible for these differences.

5) There are some small peaks in Figure 5. Are they from contaminants? If so, the authors should clarify this in the paper.

As you can see from Figure 5, there are some weak small peaks except the characteristic peaks of gaseous SO_2. These small peaks are due to H_2O. H_2O molecules can evaporate slowly from the humid surface of FN sample which is placed in the White cell. These small peaks can be clearly observed when the concentration of SO_2 is low, while they are not obvious when high SO_2 concentration is used. Please also refer to the literature published by Zhang et al.(2006).

6) It seems to me that N_2O has not reaches a plateau in Figure 6f.

Sorry, we also feel that the statement is too strong.

The statement for the trend in N_2O concentrations is mainly based on the fitting curve shown in Figure 6f. We change the expression in the revised manuscript:

Page 24, line 532 (page 11596, line 29), "…gradually increases and ultimately reaches a constant" is replaced by "…gradually increases and approaches a constant".

7) Page 11599, line 20-23. Please clarify that the DRIFTS cell is coupled with a temperature control system in the experimental section. It is not clear when and why a vacuum was applied to the DRIFTS cell. The authors should describe the procedure in more details here or in the experimental section.

We accept this suggestion. In the experimental section, we further clarify that the DRIFTS cell is coupled with a temperature control system.

Page 7, line 137 (page 11582, line 9), “The DRIFTS sample cell is coupled with a temperature controller.” is inserted.

Page 7, line 138 (page 11582, line 10). “a” is replaced by “the”.

For the question about when and why a vacuum was applied to the DRIFTS cell, we are very sorry for our incorrect writing which led to your confusion. During the experiments, a vacuum wasn’t applied to the in situ chamber in order to prevent the sample particles from being brought out. Based on this question, we have made some corrections:

Page 27, line 606 (page 11599, line 20-21). This sentence is revised to “In order to prevent the sample particles from being brought out from the in situ chamber, a vacuum wasn’t applied during these experiments.”;

Page 28, line 610 (page 11599, line 24). A comma is inserted before “and a background spectrum…”.

8) Surface-adsorbed water usually greatly affects heterogeneous reaction. In this study, all of the samples were placed in a desiccator at 68% RH before use. But in DRIFTS experiment, the chamber was purged with argon (dry?) for 1 h, and then the gaseous reactants (dry?) were introduced into the chamber. I assume that these processes would cause a loss of surface adsorbed water and DRIFTS spectra could provide information regarding this. The authors should show and discuss the band attributed to surface adsorbed water (around 1640 cm^{-1}). This may provide more information regarding how water is involved in the heterogeneous reaction.

In the experimental section (page 11581, line 16-18), we mentioned that gaseous oxygen, argon and SO_2 were introduced into reaction chamber through an air-dryer. Therefore, these gases are dried. Just as you think, the introduction of the dried gases into the chamber will cause a loss of surface adsorbed water. Fig. R4 shows a loss of surface adsorbed water during the purge process (here we zoom in on major areas). As can be seen from Fig. R4, the loss of surface adsorbed water is rapid at an early stage, but the loss is becoming smaller and smaller with the purge time. After about 40 min, the loss of water is almost stopped. On the whole, after this purge process, the water loss is low and some water or water molecule layers (from surface adsorbed water, water-solvated nitrate, etc.) remain existed on the surface.

Generally, the loss of water during the reaction will also be caused by the dried gas stream, and a negative absorption peak around 1640 cm^{-1} will be observed. However, the loss of surface adsorbed water (around 1640 cm^{-1}) is not easy to be observed after the introduction of the gaseous reactant SO_2 (using a background spectrum measured on the powder sample purged for 1 h, Fig. R5), which indicates less water loss (also see Fig. 3 in the manuscript). The reasons may be as follows.

(1) The absorption peaks of adsorbed nitric acid and different nitric acid-water complexes are superimposed on the absorption band of the surface-adsorbed water (around 1640 cm^{-1}), and the former increases in intensity as the reaction time increases. But compared with the absorption peaks of adsorbed nitric acid and different nitric acid-water complexes, the absorption band around 1640 cm^{-1} has a little increase, indicating less water loss.

(2) During the reaction, water may be difficult to leave the particle surface due to the presence of nitrate and nitric acid product. For example, water is bound by water-solvated nitrate, and the solvated nitrate may become a water reservoir for reaction.

(3) Water may be produced during the reaction of SO_2 with surface hydroxyls. Please refer to our proposed mechanism in the manuscript.

Besides, some previous studies also found that adsorption bands due to surface adsorbed water at 1640 cm^{-1} were fairly weak or increased in intensity with reaction time. For example, Wu et al. (2013) studied the heterogeneous reaction of SO_2 on α-Fe_2O_3 and their result showed that the band around 1640 cm^{-1} increased in intensity with time. Ramazan et al. (2006) studied the heterogeneous hydrolysis of NO_2 using ATR spectrum and their results showed that surface water absorption peak around 1640 cm^{-1} changed little. However, Angelini et al. (2007) studied heterogeneous reactions of gaseous NO_2 on kaolinite and their results showed that the band around 1640 cm^{-1} increased in intensity with reaction time.

Appropriate revisions have been made in the revised manuscript, and please refer to the answers to the question (5) and (13) in detailed comments of anonymous referee #1.

Specific comments:

1) Page 11578, line 4, on heterogeneous reactions

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

Page 2, line 22, “the” is deleted.

2) Page 11578, line 6, at 298 k are investigated

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

Page 2, line 24, “were” is replaced by “are”.

3) Page 11578, line 9, in heterogeneous reactions of

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

Page 2, line 27, “the” is deleted.

4) Page 11578, line 11-12, delete ‘revealing that…..to sulfate‘

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

Page 2, line 29-30, “revealing that…..to sulfate” is deleted.

5) Page 11578, line 12-14, rephrase the sentence ‘the results indicate…..on hematite’. Redundant words in ‘favor the enhancement’

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

Page 2, line 30-32, the sentence “the results indicate…..on hematite” is replaced by “The results indicate that low to moderate amounts of nitrate significantly enhance the reactivity of hematite-nitrate mixtures, the uptake of SO_2 and the formation of sulfate on hematite.”

6) Page 11578, line 16, change ‘average’ to ‘averaged’. Same applied to page 11593, line 3, line 7; page 11599, line5, line 28; page 11604, line 27; Figure 4 & 9 in captions

and Y-axis labels.

The sulfate formation rate was measured through parallel experiments, and the rate was the averaged value of these parallel experiments. This is a commonly used research method. Therefore, for the sulfate formation rate in the revised manuscript, we no longer emphasize “averaged”.

Page 2, line 33, “average” is deleted;

Page 19, line 421, according to the answer to comment 4, Fig. 4 is replaced by Table 2, and corresponding “average” is removed.

Page 19, line 425, Fig. 4 is replaced by Table 2, and corresponding “average” is removed.

Page 27, line 590, we accept this suggestion, and change “average particle size” to “averaged particle size”.

Page 28, line 614, “the average formation rate of sulfate at 423 K…” is replaced by “the sulfate formation rates at 373 and 423 K…”.

Page 34, line 744, “average sulfate formation rate” is replaced by “sulfate formation rate”.

Figure 4 & 9 in captions and Y-axis labels, Fig. 4 is removed. Appropriate revisions have been made in Fig. 9.

7) Page 11579, line 5, in cloud and fog droplets

We accept this suggestion:

Page 3, line 51, corresponding revision has been made in the revised manuscript.

8) Page 11579, line 12, in cloud and fog droplets are insufficient to

We accept this suggestion:

Page 3, line 58, corresponding revision has been made in the revised manuscript.

9) Page 11579, line 17, on aerosols has therefore received increasing attention

We accept this suggestion:

Page 3, line 63, corresponding revision has been made in the revised manuscript.

10) Page 11579, line 23, the underlying mechanisms of sulfate formation

We accept this suggestion:

Page 4, line 68-69, corresponding revision has been made in the revised manuscript.

11) Page 11579, line 26, but little attention has been paid

We accept this suggestion:

Page 4, line 71-72, corresponding revision has been made in the revised manuscript.

12) Page 11580, line 5-6, change their sizes, optical and hygroscopic properties as well as lifetime in the atmosphere

We accept this suggestion:

Page 4, line 79-80, corresponding revision has been made in the revised manuscript

13) Page 11580, line 14, has implications for global climate as well as carbon and nitrogen cycles

We accept this suggestion:

Page 4, line 88, corresponding revision has been made in the revised manuscript.

14) Page 11580, line 19, enhances hydroscopic properties of original particles

We accept this suggestion:

Page 5, line 92-93, corresponding revision has been made in the revised manuscript.

15) Page 11580, line 18-22, split the sentence into two

We accept this suggestion, and corresponding revision has been made in the revised manuscript:

Page 5, line 92-95, the revised sentences are as follows.

“Surface nitrate enhances hygroscopic properties of original particles and, in turn, changes their physicochemical properties (Hoffman et al., 2004). This will inevitably impact their chemical reactivity, and therefore lead to a remarkable difference in their heterogeneous chemistry.”

16) Page 11580, line 22, little attention has

We accept this suggestion:

Page 5, line 95-96, corresponding revision has been made in the revised manuscript.

17) Page 11580, line 23, on heterogeneous reactions of

We accept this suggestion:

Page 5, line 96, corresponding revision has been made in the revised manuscript.

18) Page 11581, line 3-4, The results reveal a potential pathway of sulfate formation

We accept this suggestion:

Page 5, line 105-110, according to your and the anonymous referee #1's suggestion [question (2) in the detailed comments], corresponding revision has been made in the revised manuscript. The original part is revised to "The results reveal a potential pathway of sulfate formation in the troposphere and the significant contribution of particulate nitrate for the conversion of SO_2 and the enhanced formation of sulfate in the atmosphere.".

19) Page 11581, line 8, will also help to elucidate the formation

This sentence has been removed in the manuscript according to the anonymous referee #1's suggestion. Please also refer to the answer to question 18.

20) Page 11581, line 19, nitrate on heterogeneous reactions

We accept this suggestion:

Page 6, line 121, corresponding revision has been made in the revised manuscript.

21) Page 11581-11582, all of the prepared samples were kept

We accept this suggestion:

Page 6, line 128-129, corresponding revision has been made in the revised manuscript.

22) Page 11582, line 6, were recorded using a Nicolet

We accept this suggestion:

Page 7, line 134, corresponding revision has been made in the revised manuscript.

23) Page 11582, line 8, delete redundant word ', just'. Same applied to page 11592, line 22; page 11596, line 26

We accept this suggestion, and corresponding revisions have been made in the revised manuscript:

Page 7, line 136; Page 19, line 413; Page 24, line 529.

24) Page 11582, line 9-10, A 30-mg sample was place into the ceramic sample holder

We accept this suggestion:

Page 7, line 137, corresponding revision has been made in the revised manuscript.

25) Page 11583, line 4, before a sample

We accept this suggestion:

Page 8, line 157, corresponding revision has been made in the revised manuscript.

26) Page 11583, line 5, A 30-mg sample was placed in a

We accept this suggestion:

Page 8, line 158, corresponding revision has been made in the revised manuscript.

27) Page 11583, line 13-14, were recorded using a

We accept this suggestion:

Page 8, line 166, corresponding revision has been made in the revised manuscript.

28) Page 11583, line 16-17, A single-beam spectrum collected prior to the SO_2 exposure was used as the reference spectrum

We accept this suggestion:

Page 8, line 168-169, corresponding revision has been made in the revised manuscript.

29) Page 11583, line 17-18, In order to trace gaseous products, a long reaction time (up to 20 h) was adopted in some experiments.

We accept this suggestion:

Page 8, line 169-171, corresponding revision has been made in the revised manuscript.

30) Page 11583, line 19, SO_2 have a

We accept this suggestion:

Page 8, line 171, corresponding revision has been made in the revised manuscript.

31) Page 11585, line 6-7, A blank analysis was performed prior to running a sample Analysis

We accept this suggestion:

Page 10, line 211-212, corresponding revision has been made in the revised manuscript.

32) Page 11585, line 18, delete ‘as can be seen in Fig. 1a,’

We accept this suggestion:

Page 10, line 222, corresponding revision has been made in the revised manuscript.

33) Page 11585, line 21, assigned to adsorbed bisulfate

We accept this suggestion:

Page 11, line 225, corresponding revision has been made in the revised manuscript.

34) Page 11586, line 6-7, The peak at 1335 cm^{-1}

We accept this suggestion:

Page 11, line 234, corresponding revision has been made in the revised manuscript.

35) Page 11586, line 10, peak fitting using a combination of

We accept this suggestion:

Page 11, line 238, corresponding revision has been made in the revised manuscript.

36) Page 11586, line 12, 1158 cm^{-1} simultaneously increase

We accept this suggestion:

Page 11, line 240, corresponding revision has been made in the revised manuscript

37) Page 11586, line 15, and then slightly decreases in intensity

We accept this suggestion:

Page 11, line 242-243, corresponding revision has been made in the revised manuscript.

38) Page 11586, line 18, bisulfate and sulfate adsorbed on

We accept this suggestion:

Page 11, line 245, corresponding revision has been made in the revised manuscript.

39) Page 11586, line 19, spell out ‘PDFTIR’

We accept this suggestion:

Page 12, line 246, corresponding revision has been made in the revised manuscript. That is, potential difference Fourier transform infrared spectroscopy.

40) Page 11586, line 22, after drying of a hematite layer

We accept this suggestion:

Page 12, line 249, corresponding revision has been made in the revised manuscript. That is, “the” is replaced by “a”.

41) Page 11586, line 24 He suggested that the conversion

We accept this suggestion:

Page 12, line 251, corresponding revision has been made in the revised manuscript.

42) Page 11586, line 28, sulfate changed from

We accept this suggestion:

Page 12, line 254-255, corresponding revision has been made in the revised manuscript.

43) Page 11586, line 29, on {012} and {1m0} surfaces

We accept this suggestion:

Page 12, line 256, corresponding revision has been made in the revised manuscript.

44) Page 11587, line 1, and they suggested

We accept this suggestion:

Page 12, line 257, corresponding revision has been made in the revised manuscript.

45) Page 11587, line 3, delete "obviously". Please delete most "obviously" and "clearly" in the paper. They are redundant words.

We accept this suggestion, and corresponding revisions have been made in the revised manuscript:

Page 12, line 259, delete "obviously";

Page 14, line 302 (page 11588, line 18), "obviously" is replaced by "Therefore";

Page 20, line 426 (page 11593, line 8), this section is modified according to your comment 4 in general comments.

Page 26, line 563 (page 11598, line 4), delete "obviously";

Page 28, line 613 (page 11599, line 27), delete "obviously".

For deleting "clearly":

Page 14, line 310 (page 11588, line 27);

Page 15, line 329 (page 11589, line 17);

Page 18 line 387 (page 11591, line 22);

Page 27, line 595 (page 11599, line 9);

Page 29, line 639 (page 11600, line 28);

Page 34, line 742 (page 11604, line 25).

46) Page 11587, line 4, remains controversial

We accept this suggestion:

Page 12, line 259-260, corresponding revision has been made in the revised manuscript.

47) Page 11587, line 15, along with consumption of

We accept this suggestion:

Page 13, line 270, according to the anonymous referee #1's suggestion (comment 8 in the detailed comments), the revised sentence is placed into supplemental information (please see Section S3).

48) Page 11587, line 24, in this region because of the increase of

We accept this suggestion:

Page 13, line 279, corresponding revision has been made, and according to the anonymous referee #1's suggestion, the revised sentence is placed into supplemental information (please see Section S6).

49) Page 11587, line 26, HSO_3^- and SO_3^{2-}. Same applied to page 11595, line 12; page 11597, line 11; page 11601, line 16; page 11602, line 13

We accept this suggestion, and corresponding revisions have been made in the revised manuscript:

Page 13, line 281-282 (Page 11587, line 26): according to the anonymous referee #1's suggestion, the revised sentence is placed into supplemental information (please see Section S6).

Page 22, line 487 (page 11595, line 12-13);

Page 25, line 543 (page 11597, line 11);

Page 30, line 655 (page 11601, line 15);

Page 31, line 679 (page 11602, line 12-13).

50) Page 11588, line 1, shows typical spectra

We accept this suggestion:

Page 13, line 285, corresponding revision has been made in the revised manuscript.

51) Page 11588, line 2, delete 'In Fig. 1b, '

We accept this suggestion:

Page 13, line 286, corresponding revision has been made in the revised manuscript.

52) Page 11588, line 4-5 be assigned to surface-coordinated

We accept this suggestion:

Page 13, line 288, corresponding revision has been made in the revised manuscript.

53) Page 11588, line 15, delete ‘compared with that of hematite,’

We accept this suggestion:

Page 14, line 298, corresponding revision has been made in the revised manuscript.

54) Page 11588, line 17, delete ‘as the reaction proceeds,’

We accept this suggestion:

Page 14, line 301, corresponding revision has been made in the revised manuscript.

55) Page 11588, lien 23-24, is composed of three major peaks at 1207, 1155 and 1094 cm^{-1}.

We accept this suggestion:

Page 14, line 306-307, corresponding revision has been made in the revised manuscript.

56) Page 11589, line 6, are further oxidized in

We accept this suggestion:

Page 15, line 318-319, corresponding revision has been made in the revised manuscript.

57) Page 11589, line 11-12, should specify ‘the same experiment’. Experiment with pure hematite or FN-24?

We accept this suggestion, and we specify “the same experiment” in the revised manuscript:

Page 15, line 324, that is, “experiment with FN-24”.

58) Page 11589, line 12, Figure 3 shows DRIFTS

We accept this suggestion:

Page 15, line 324, corresponding revision has been made in the revised manuscript.

59) Page 11589, line 13, delete ‘increasing’

We accept this suggestion:

Page 15, line 325, corresponding revision has been made in the revised manuscript.

60) Page 11589, line 14, delete ‘in the same experiment. As shown in Fig. 3. ‘

We accept this suggestion:

Page 15, line 325-326, corresponding revision has been made in the revised manuscript.

61) Page 11590, line 2, delete ‘product’

We accept this suggestion:

Page 16, line 339, “products” is deleted in the revised manuscript.

62) Page 11590, line 4, at 1716, 1697, 1686 and 1676 cm^{-1}

We accept this suggestion:

Page 16, line 341, corresponding revision has been made in the revised manuscript.

63) Page 11590, line 8-9, reverse the listing order as well

We accept this suggestion:

Page 16, line 345-346, corresponding revision has been made in the revised.

64) Page 11590, line 10-11, This result confirms that adsorbed HNO_3

We accept this suggestion:

Page 16, line 347-348, corresponding revision has been made in the revised manuscript.

65) Page 11590, line 12, The formation of HNO_3-H_2O complexes

We accept this suggestion:

Page 16, line 349, corresponding revision has been made in the revised manuscript.

66) Page 11590, line 14-15, no gas phase HNO_3 was observed in White cell-FTIR experiments as discussed later.

We accept this suggestion:

Page 16, line 351-352, corresponding revision has been made in the revised manuscript.

67) Page 11590, line 15-16, molecularly adsorbed nitric acid.

We accept this suggestion:

Page 16, line 352, corresponding revision has been made in the revised manuscript.

68) Page 11590, line 17, in previous reports

We accept this suggestion:

Page 16, line 353-354, corresponding revision has been made in the revised manuscript.

69) Page 11590, line 26, compared to previous studies

70) Page 11590, line 27-29, rephrase ‘which may suggest…..interactions with H_2O’. change ‘is interacting with’ to ‘interacts with’. Either delete ‘may’ or ‘perhaps’

71) Page 11591, line 1-3, particle surface with nitric acid and H_2O present. This is consistent with the fact that no gas phase N_2O_4 was detected in While cell-FTIR experiments as discussed later.

For 69), 70) and 71), according to your comment 2) in general comments and these suggestions, we revise this part (page 16-17, line 358-368). Please refer to the answer to the question 2) in general comments.

72) Page 11591, line 12, are stretching vibration modes of isolated surface

We accept this suggestion:

Page 17, line 376-377, corresponding revision has been made in the revised manuscript.

73) Page 11591, line 13, ions of octahedral sites and tetrahedral sites

We accept this suggestion:

Page 17, line 378, corresponding revision has been made in the revised manuscript.

74) Page 11591, line 14, that surface OH groups

We accept this suggestion:

Page 17, line 379, corresponding revision has been made in the revised manuscript.

75) Page 11591, line 15, are reaction active sites

We accept this suggestion:

Page 17, line 380, corresponding revision has been made in the revised manuscript.

76) Page 11591, line 17, slowly increases in intensity

We accept this suggestion:

Page 17, line 382, corresponding revision has been made in the revised manuscript.

77) Page 11591, line 21, surface-adsorbed HNO_3 discussed earlier.

We accept this suggestion:

Page 18, line 386, corresponding revision has been made in the revised manuscript.

78) Page 11591, line 22, delete ‘mentioned above clearly’

We accept this suggestion:

Page 18, line 387, corresponding revision has been made in the revised manuscript.

79) Page 11592, line 3-4, All of the DRIFTS experiments

We accept this suggestion:

Page 18, line 394-395, corresponding revision has been made in the revised manuscript.

80) Page 11592, line 13, of different reaction product

We accept this suggestion:

Page 19, line 404, corresponding revision has been made in the revised manuscript.

81) Page 11592, line 14, one another, the peaks were deconvoluted before integration in some experiments.

We accept this suggestion:

Page 19, line 405, corresponding revision has been made in the revised manuscript.

82) Page 11592, line 16, since O_2 was in great excess compared to SO_2

We accept this suggestion:

Page 19, line 407-408, corresponding revision has been made in the revised.

83) Page 11593, line 4, delete 'as shown in Fig. 4,'

84) Page 11593, line 10, delete 'under the same reaction conditions'

85) Page 11593, line 13-14, the reaction behavior of SO_2 adsorbed on hematite

On page 19-20, line 421-432 (page 11593, line 3-14), based on the comment 4) in your general comments, this part has been modified in the revised manuscript (including the introduction of the uptake coefficient calculation method, the calculated results and corresponding discussions). Therefore, for 83), 84) and 85), we accept these suggestions as far as possible in the revised manuscript.

86) Page 11593, line 15, should receive close attention

We accept this suggestion:

Page 20, line 433, corresponding revision has been made in the revised manuscript.

87) Page 11593, line 16, in ambient particles

We accept this suggestion:

Page 20, line 433-434, corresponding revision has been made in the revised manuscript.

88) Page 11593, line 19, and possible gaseous

We accept this suggestion:

Page 20, line 437, corresponding revision has been made in the revised manuscript.

89) Page 11593, line 22, from exposure of the FN-24 sample

We accept this suggestion:

Page 20, line 440, corresponding revision has been made in the revised manuscript.

90) Page 11594, line 1-2, but different rates of SO_2 consumption

We accept this suggestion:

Page 20, line 447, corresponding revision has been made in the revised manuscript.

91) Page 11594, line 5, and the FN-24 sample

We accept this suggestion:

Page 21, line 450-451, corresponding revision has been made in the revised manuscript.

92) Page 11594, line 6, with the rate of sulfate formation observed in DRIFTS experiments.

We accept this suggestion:

Page 21 line 451-452, appropriate revision has been made and in the revised manuscript we use “with that observed in DRIFTS experiments.”.

93) Page 11594, line 10, to lower concentrations of SO_2.

We accept this suggestion:

Page 21, line 457-458, corresponding revision has been made in the revised manuscript.

94) Page 11594, line 11, although adsorbed HNO_3

We accept this suggestion:

Page 21, line 458, corresponding revision has been made in the revised manuscript.

95) Page 11594, line 13, observed in White cell-FTIR

We accept this suggestion:

page 21, line 459, corresponding revision has been made in the revised manuscript.

96) Page 11594, line 15, from exposure of the FN-90 sample

We accept this suggestion:

Page 21, line 462, corresponding revision has been made in the revised manuscript.

97) Page 11594, line 16, was obtained

We accept this suggestion:

Page 21, line 463, corresponding revision has been made in the revised manuscript.

98) Page 11594, line 25, the degradation of primary

We accept this suggestion:

Page 22, line 472, corresponding revision has been made in the revised manuscript.

99) Page 11595, line 4, delete ‘detectable’. Same applied to line 8-9

We accept this suggestion, and corresponding revisions have been made in the revised manuscript:

Page 22, line 478, delete “detectable”. Same applied to page 22, line 483.

100) Page 11595, line 5, It is possible that gaseous NO

We accept this suggestion:

Page 22, line 480-481, corresponding revision has been made in the revised manuscript.

101) Page 11595, line 14-18, split into two sentences. ‘many more reduced’ change to ‘much more reduced’, ‘longer’ change to ‘long’

We accept this suggestion:

Page 22, line 489-492, corresponding revisions have been made in the revised manuscript: “On the other hand, the high concentration of SO_2 means that there are much more reduced S(IV) species existing on the sample surface than those formed from the low concentration of SO_2. This also implies that HONO will be observed within a long reaction time if the high concentration of SO_2 is used.”

102) Page 11595, line 25, surface of FN samples placed in the White cell.’

We accept this suggestion:

Page 23, line 499, corresponding revision has been made in the revised manuscript.

103) Page 11596, line 1, White cell-FTIR and DRIFTS techniques

We accept this suggestion:

Page 23, line 504, corresponding revision has been made in the revised manuscript.

104) Page 11596, line 2, show no detectable gas phase products, indicating

We accept this suggestion:

Page 23, line 505, corresponding revision has been made in the revised manuscript.

105) Page 11596, line 20, the contribution of HONO by this

We accept this suggestion:

Page 24, line 523, corresponding revision has been made in the revised manuscript.

106) Page 11596, line 25, mixtures at both low and high SO_2

We accept this suggestion:

Page 24, line 528, corresponding revision has been made in the revised manuscript.

107) Page 11596, line 26, delete 'gradually'

We accept this suggestion:

Page 24, line 530, corresponding revision has been made in the revised manuscript.

108) Page 11597, line 25, at room temperature

We accept this suggestion:

Page 25, line 556, corresponding revision has been made in the revised manuscript.

109) Page 11598, line 1, 'strong acidity' is vague, should at least provide a range of pH

We accept this suggestion:

Page 25, line 560, "the pH was about 1" is added.

110) Page 11599, line 1-2, shows SEM images

We accept this suggestion:

Page 27, line 587, corresponding revision has been made in the revised manuscript.

111) Page 11599, line 5-6, delete 'After comparing these images, we notice that'

We accept this suggestion:

Page 27, line 591, corresponding revision has been made in the revised manuscript.

112) Page 11600, line 12, on hematite-nitrate mixtures

We accept this suggestion:

Page 28, line 626, corresponding revision has been made in the revised manuscript.

113) Page 11603, line 3, strongly with water and adsorbed HNO_3

We accept this suggestion:

Page 31, line 695, corresponding revision has been made in the revised manuscript.

114) Page 11603, line 6, This can explain small amounts of

We accept this suggestion:

Page 32, line 698, corresponding revision has been made in the revised manuscript.

115) Page 11603, line 25, delete ‘at last’

We accept this suggestion:

Page 32, line 714, corresponding revision has been made in the revised manuscript.

116) Page 11603, line 26, during heterogeneous hydrolysis

We accept this suggestion:

Page 32, line 716, corresponding revision has been made in the revised manuscript.

117) Page 11604, line 24, delete ‘Compared with hematite solely, ’

We accept this suggestion:

Page 34, line 741, corresponding revision has been made in the revised manuscript.

118) Page 11605, line 2, on particle surfaces and

We accept this suggestion:

Page 34, line 746, corresponding revision has been made in the revised manuscript.

119) Page 11605, line 23, change comma to period

We accept this suggestion:

Page 35, line 766, corresponding revision has been made in the revised manuscript.

120) Page 11615, Fig. 2 caption, Peak fitting of the

We accept this suggestion:

Page 49, line 1030, corresponding revision has been made in the revised manuscript.

121) Page 11618, Fig. 5 caption, delete space between 21 and %. Same applied to Fig. 6 and 7

We accept this suggestion, and corresponding revisions have been made in the revised manuscript:

Page 52, line 1062 (page 11618);

page 53, line 1077 (page 11619);

page 54, line 1092 (page 11620).

Anonymous Referee #3

The authors utilized online spectroscopic and offline chromatographic approach to investigate the effects of nitrate on the heterogeneous uptake of SO_2 on hematite. There are several issues in this work.

Firstly, the substrates have been known to play important roles in heterogeneous uptake. The author should have performed more characterization about their hematite samples.

We agree with this comment. In the manuscript, we performed XRD and BET characterization about our samples. We are also considering performing some other characterization about the hematite sample, which will help to obtain more information about our samples. In the answer to the comments of anonymous referee #1 and #2, we give some other information about the substrates. For your convenience we put the main contents below:

(1) In our study, the nitrate-hematite mixtures and pure nitrate are still loose fine powders after they are equilibrated at 68% RH for 48 h, and the nitrate and hematite are not immersed in a solution after the equilibration (for example, FN-24 after equilibration. Please see Fig. R1).

(2) The loss of surface adsorbed water during the purge process and the actual sulfur oxidation experiments (The anonymous referee #1 and #2 concerns about the loss of water during the experiments. In the answers to the first question in general comments of anonymous referee #1 and the question 8 in general comments of anonymous referee #2, we give some experimental results and discuss the loss of surface adsorbed water during the purge process and the actual sulfur oxidation experiments. Please refer to these answers, and also see Fig. R4 and R5.).

During purge process, we found that the loss of water is almost stopped after about 40 min, and on the whole, the loss of water is low. The loss of surface adsorbed water (around 1640 cm^{-1}) is not easy to be observed after the introduction of the gaseous reactant SO_2 (using a background spectrum measured on the powder sample which was purged with argon for 1 h), which indicates less water loss. These results may be attributed to the presence of nitrate. That is, the water-solvated nitrate bound water molecules on the particle surface due to its hygroscopic properties, and the solvated nitrate may become a water reservoir for reaction. Weak water loss will favor the redox cycles of Fe^{3+}/Fe^{2+} and the heterogeneous conversion of SO_2.

(3) X-ray diffraction analyses of pure hematite, humid FN-24 and FN-48. The results are shown in Fig.R2.

We performed X-ray diffraction analyses of pure hematite, humid FN-24 and FN-48. The results are shown in Fig. 4. The crystalline peaks at 29.65 °, 31.9 °, 39.0 ° and 47.9 ° can be identified as the characteristic reflections of $NaNO_3$. No amorphous sodium nitrate was present because there was no broad amorphous peak in the 20 ° - 40 ° range. In addition, as can be seen from Fig. R2, except for the crystalline peaks of hematite and nitrate, no other crystalline phases are formed, which indicated that the FN sample we used was a mixture of hematite and sodium nitrate, and also indicated that no secondary processes occurred on the hematite surface during the sample preparation and the subsequent sample equilibration at 68% RH.

Corresponding revisions have been made in the revised manuscript:

(1) In the supporting information, Fig. S1 is replaced by Fig. R2 mentioned above, and the corresponding explanations are presented.

(2) Page 6, line 130 (Page 11582, line 2), "Powder X-ray diffraction indicated that no secondary processes occurred on the hematite surface during the sample preparation and the subsequent sample equilibration (see Fig. S1 in the Supplement)." is added in the revised manuscript.

In addition, we may further carry out the studies on (1) nitrate ions on the surface of hematite or different crystal faces by other characterization techniques, just as previously reported (e.g. Barron, et al. 1996; Watanabe, et al., 1994); (2) hygroscopic behavior of the nitrate-hematite mixture particles, and so on.

Secondly, the authors intended to understand how nitrate affects heterogeneous SO_2 uptake, but there is no uptake coefficient data reported in this work. The IR spectra actually have shown spectral evolution of different absorption peaks. I do not understand why the authors avoided using their infrared data to derive reaction kinetics. Note that they did use sulfate formation rate as a semiquantitative approach for the uptake measurements. This is very problematic because it is not always true that reactant (SO_2) is completely converted to products (sulfate).

In the original manuscript, we point out that a further analysis for reaction uptake coefficients by DRIFTS is difficult because the evaluation of the diffusion depth and total actual reaction sample area are unavailable in this study, and hence we did not give the uptake coefficient data. However, as you know, in many previously reported studies, upper and lower limits of uptake coefficients can be estimated using the geometric area of the sample holder (assuming SO_2 only reaches the surface) and the BET surface area of the sample (assuming SO_2 can diffuse into the entire sample). Therefore, according to your and the anonymous referee #2's suggestions, we use the new selected initial stage (0-60 min) to recalculate the sulfate formation rates and the two kinds of uptake coefficients of SO_2 on hematite and the hematite-nitrate mixtures (see Table R3, or Table 2 in the revised manuscript). Corresponding revisions have already been made in the revised manuscript. For example, replace Fig.4 by Table 2, add the introduction of the calculation method of uptake coefficient, the calculated results and corresponding discussions, etc. Please refer to the answer to question 4 in the general comments of the anonymous referee #2 and the revised manuscript.

Except for the different substrates, our DRIFTS experiments were performed under the same conditions (e. g. 298 K, 30 mg of sample, 21% v/v O_2, constant total flow rate, the same SO_2 concentration). Meanwhile, the actually formed sulfate product was measured. Based on the measured sulfate, we calculated the sulfate formation rate. The directly calculated sulfate formation rate and the subsequent calculated uptake coefficients in the revised manuscript should be able to reflect the reactivity of the different substrates, as reported previously.

Secondary processes could occur on the hematite surface and more importantly various hematite surfaces could lead to drastically different product formation. Again, more information about their hematite sample is critically needed.

Please refer to the response to the first comment.

Moreover, for a typical uptake study, experiments are conducted under a pseudo-first-order condition. It is unclear to me that how their experiment conditions meet such a requirement.

The conclusion that the heterogeneous oxidation of SO_2 on the hematite-nitrate mixture (FN sample) is a pseudo-first-order reaction is drawn from our experimental results. In the DRIFTS experiments, we performed the experiments with different SO_2 concentrations (conditions: 298 K, 30 mg of sample, 21% v/v O_2, constant total flow rate with a preset concentration of SO_2).

The kinetics of the reaction of SO_2 with the FN particle surface may be described by the general equation:

$d[SO_4^{2-}]/dt = k[SO_2]^m[O_2]^n\{hematite\}^p[NaNO_3]^q$

Concentrations marked with { } indicate reactive surface species, whereas $[SO_2]$, $[O_2]$ and $[NaNO_3]$ indicate the concentrations of SO_2, O_2 and $NaNO_3$. k is the rate constant, and m, n, p, q are the reaction orders for SO_2, O_2, hematite, and $NaNO_3$, respectively.

The gas-phase concentrations of the reactive gases in a continuous flow were kept constant during the DRIFTS experiments and since O_2 was in great excess compared to SO_2, the concentration of O_2 could be regarded as constant. The number of sulfate ions formed at the initial stage of reaction is generally considered to be small relative to the number of reactive surface species, and thus the reactive surface species on hematite at initial stage can be assumed to be constant (Börensen, et al., 2000). In order to simplify this analysis, we also assumed $[NaNO_3]$ be constant. Therefore, the reaction order can be determined from a bilogarithmic plot of initial rate of sulfate formation ($\log(d[SO_4^{2-}]/dt)$) vs. the concentration of SO_2 ($\log[SO_2]$):

$\log(d[SO_4^{2-}]/dt)=\log k+ m \log[SO_2] + n \log[O_2] + p \log\{hematite\} + q \log[NaNO_3]$

The sulfate formation rate $d[SO_4^{2-}]/dt$ was obtained from the slope of the initial linear portion (0-60 min) in the curve of sulfate formation as a function of time, and no saturation effects on sulfate formation are observed.

For the mixture such as FN-24 used in this study, the bilogarithmic plot presented a linear relationship with a slope of about 1.09, which indicates a reaction order of 1 for SO_2. This result also indicates that the assumptions in the analysis of reaction order are valid.

In our study, the heterogeneous uptake and oxidation of SO_2 on particle surfaces were also performed by using in situ White cell-FTIR technique (reaction conditions: room temperature, 30 mg of sample, 21% v/v O_2, different initial concentrations of SO_2). Therefore, the reaction order with respect to SO_2 was also examined from White cell-FTIR experimental data by examining the rates of SO_2 decay (deducting blank value obtained from blank experiment). We found that the plot of $\ln[SO_2]_0/[SO_2]$ *versus* time (t) was linear, and its slope should be apparent rate constant of heterogeneous reactions of SO_2 on corresponding sample. This result further indicated that the heterogeneous reaction of SO_2 on FN sample was a pseudo-first-order reaction. For example, the apparent rate constant was determined to be 6.40×10^{-3} (linear correlation coefficient r=0.99) for uptake of SO_2 on FN-24.

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Barron, V., and Torrent, J.: Surface hydroxyl configuration of various crystal faces of hematite and goethite, J. Colloid Interface Sci., 1996, 177, 407-410.

Börensen, C., Kirchner, U., Scheer, V., Vogt, R., and Zellner R.: Mechanism and kinetics of the reactions of NO_2 or HNO_3 with alumina as a mineral dust model compound, J. Phys. Chem. A, 104, 5036-5045, 2000.

Watanabe, H., Gutleben, C. D., and Seto, J.: Sulfate ions on the surface of maghemite and hematite, Solid State Ionics, 69, 29–35, 1994.

Other revisions:

1. Page 1, line 3-4, delete the right superscript.
2. Page 1, line 5-6, delete the left superscript.
3. Page 2, line 35, “the pure nitrate” is replaced by “pure nitrate”.
4. Page 11, line 228, “Fig. 1a” is replaced by “Figure 1a”.

5. Page 13, line 276, “Fig. 1b” is replaced by “Figure 1b”.
6. Page 15, line 332 (page 11589, line 21), “Section 3.4” is replaced by “Sect. 3.4”.
7. Page 18, line 403 (page 11592, line 12), the figure is typed in wrong, we check up this figure and modify it.
8. Page 18, line 402, the italic “*vs.*” in the manuscript is corrected to “vs.”.
9. Page 19, line 412, “*versus*” is replaced by “vs.”.
10. Page 19, line 412 (page 11592, line 21), “initial formation rate of sulfate” is revised to “initial rate of sulfate formation”.
11. Page 19, line 415 (page 11592, line 25), based on the selected initial stage of reaction (0-60 min), “1.02±0.12” is replaced by the recalculated value “1.09±0.10”.
12. Page 19, line 419, “*vs.*” is replaced by “vs.”.
13. Page 21, line 450-451 (page 11594, line 5-6), “, and the FN-24 sample exhibits the highest reactivity” is deleted.
14. We choose 60 min as initial stage for the related calculation again, and hence appropriate revisions have been made in Fig. 9 (page 11622) and corresponding discussion part.

    Page 27, line 609 (page 11599, line 23), “423” is added.

    Page 27-28, line 609-625 (page 11599, line 23-page 11600, line 11), this part is modified in the revised manuscript. At the same time, we correct a mistake in calculation and add the missing 573 K data in original Fig.9. Please see the corresponding contents in the revised manuscript.
15. The numbers of reaction equations have been changed to R1, R2, …, R12.
16. The italic “*in situ*” in the manuscript is corrected to “in situ”.
17. Page 29, line 641 (page 11601, line 1), “Baltrusaitis et al., 2007; Baltrusaitis et al., 2010” is replaced by “Baltrusaitis et al., 2007, 2010”.
18. Page 31, line 687 (page 11602, line 21), “by Finlayson-Pitts *et al* and He et al (Finlayson-Pitts et al., 2003)” is replaced by “by Finlayson-Pitts et al. (2003) and Liu et al. (2012)”.
19. Page 31, line 678, “Pires et al., 1996; Pires et al., 1997” is replaced by “Pires et al.,

1996, 1997".

20. Page 36, line 799, "Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/11577/2014/ acpd-14-11577-2014-supplement.pdf." is added.
21. Page 37, line 806, italic *α*, *α*, *β*, *γ*. Same applied to page 39, line 856: *γ*
22. Page 39, line 845-847, the reference is deleted.
23. Page 41, line 883, "doi: 10.1029/2005GL022524" is added.
24. Page 44, line 945, "(Second Edition)" is replaced by "2nd edn.".
25. Page 44, line 949, "doi:10.5194/acp-11-995-2011" is added.
26. Page 44, line 957, "doi:10.5194/acp-3-2043-2003" is added.
27. Page 45, line 978, "doi:10.5194/acp-11-6593-2011" is added.
28. Page 48, line 1014-1015, "a, hematite. b, FN-24" is replaced by "**(a)** Hematite. **(b)** FN-24.".
29. Page 53, line 1077-1080, "a, b, c, d, e, f," is replaced by "**(a)**, **(b)**, **(c)**, **(d)**, **(e)**, **(f)**".
30. Page 55, line 1112-1113, bold font: **(a, b)** and **(c, d)**.

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Ramazan, K. A., Wingen, L. M., Miller, Y., Chaban, G. M., Gerber, R. B., Xantheas, S. S., and Finlayson-Pitts, B. J.: New experimental and theoretical approach to the heterogeneous hydrolysis of NO_2: Key role of molecular nitric acid and its complexes, J. Phys. Chem. A, 110, 6886-6897, 2006.

Wu, L. Y., Tong, S. R., Zhou, L., Wang, W. G., and Ge, M. F.: Synergistic effects between SO_2 and HCOOH on α-Fe_2O_3, J. Phys. Chem. A, 117, 3972-3979, 2013.

Zhang, X., Zhang, G., Chen, J., Wang, Y., Wang, X., An, Z., and Zhang, P.: Heterogeneous reactions of sulfur dioxide on typical mineral particles, J. Phys. Chem. B, 110, 12588-12596, 2006.

Fig. R1 Digital photo of FN-24 after equilibration for 48 h.

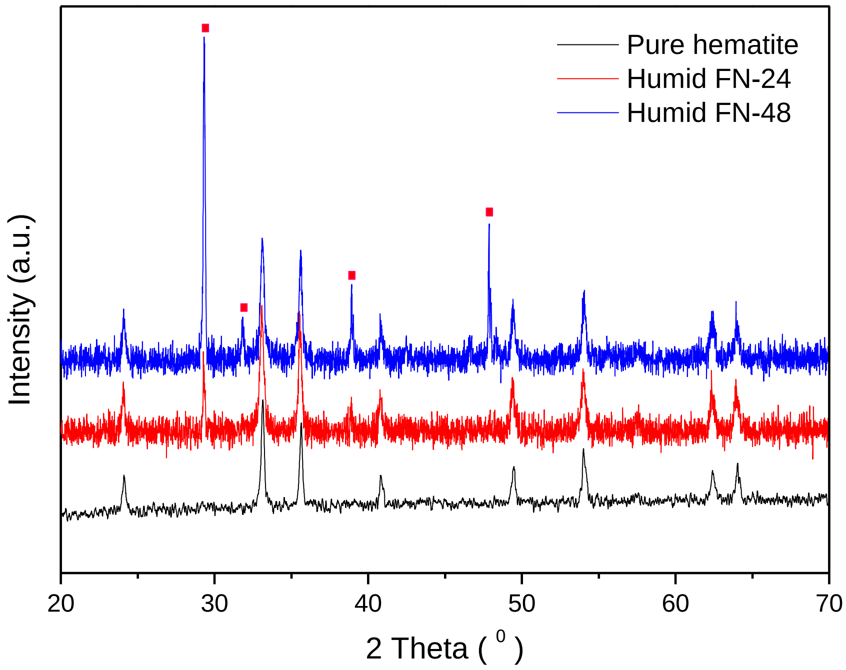

Fig. R2 X-ray diffraction patterns of pure hematite, humid FN-24 and FN-48.

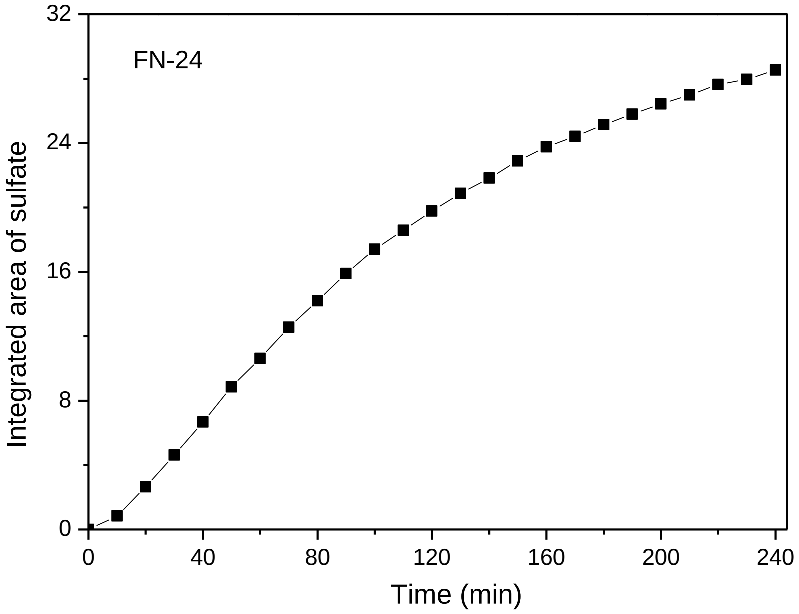

Fig. R3 Time evolution of the integrated areas of sulfate formed on FN-24.

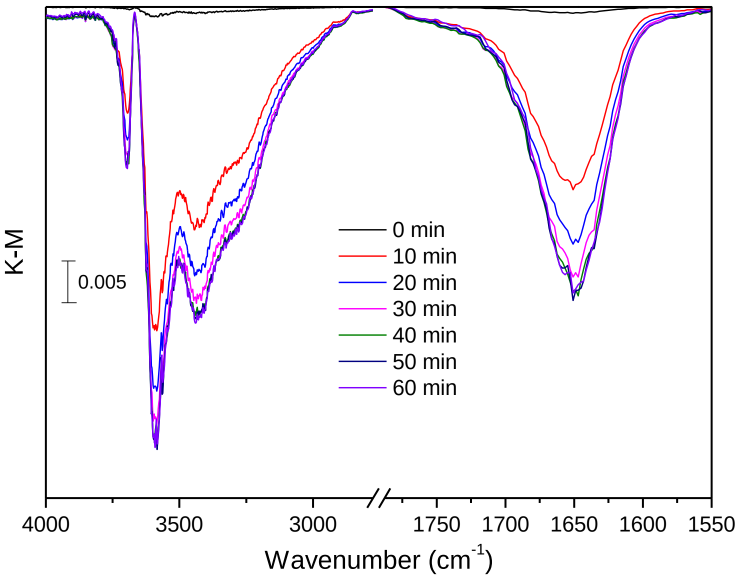

Fig. R4 loss of surface adsorbed water during purge process.

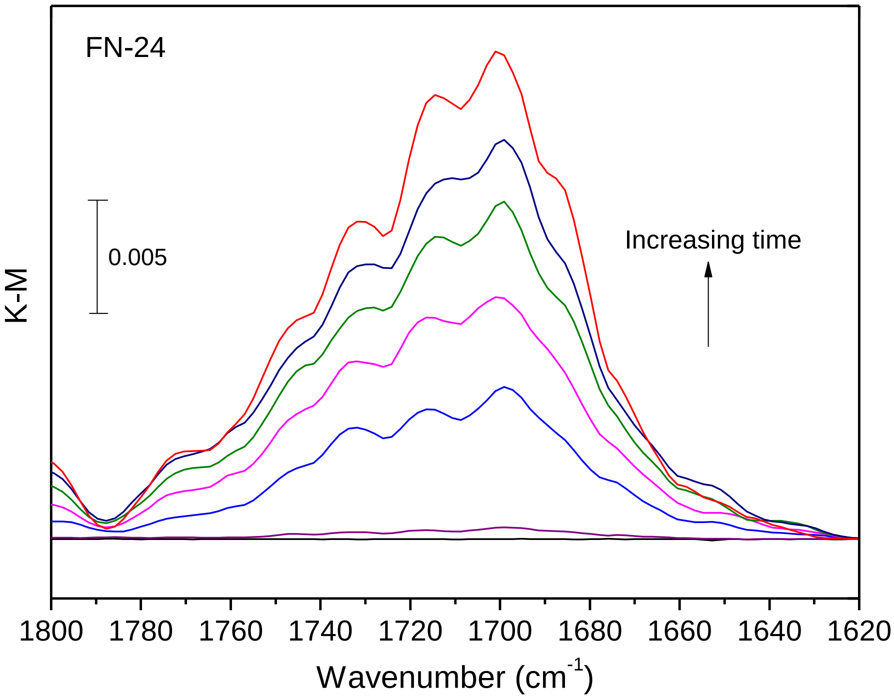

Fig. R5 Adsorption band around 1640 cm^{-1} after the introduction of gaseous reactant SO_2.