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Comment

## ***Interactive comment on “The effects of nitrate on the heterogeneous uptake of sulfur dioxide on hematite” by L. D. Kong et al.***

**Anonymous Referee #2**

Received and published: 2 June 2014

This paper investigates the effect of nitrate on the heterogeneous conversion of SO<sub>2</sub> 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<sub>2</sub> oxidation to sulfate on hematite surface. The nitrate itself can convert into surface adsorbed HNO<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> as well as gas phase N<sub>2</sub>O and HONO. The findings reveal a new SO<sub>2</sub> oxidation pathway as well as a potential source of N<sub>2</sub>O 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.

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General comments:

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

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

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.

4) Upper and lower limits of uptake coefficients can be calculated using the geometric area of the sample holder (assuming  $\text{SO}_2$  only reaches the surface) and the BET surface area of the sample (assuming  $\text{SO}_2$  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.

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

6) It seems to me that  $\text{N}_2\text{O}$  has not reaches a plateau in Figure 6f.

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.

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8) Surface-adsorbed water usually greatly affects heterogeneous reaction. In this study, all of the samples were placed in a desiccators 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<sup>-1</sup>). This may provide more information regarding how water is involved in the heterogeneous reaction.

Specific comments:

- 1) Page 11578, line 4, on heterogeneous reactions
- 2) Page 11578, line 6, at 298 K are investigated
- 3) Page 11578, line 9, in heterogeneous reactions of
- 4) Page 11578, line 11-12, delete 'revealing that. ....to sulfate'
- 5) Page 11578, line 12-14, rephrase the sentence 'the result indicate. ....on hematite'. Redundant words in 'favor the enhancement'
- 6) Page 11578, line 16, change 'average' to 'averaged'. Same applied to page 11593, line 3, line 7; page 11599, line 5, line 28; page 11604, line 27; Figure 4 & 9 in captions and Y-axis labels.
- 7) Page 11579, line 5, in cloud and fog droplets
- 8) Page 11579, line 12, in cloud and fog droplets are insufficient to
- 9) Page 11579, line 17, on aerosols has therefore received increasing attention
- 10) Page 11579, line 23, the underlying mechanisms of sulfate formation
- 11) Page 11579, line 26, but little attention has been paid
- 12) Page 11580, line 5-6, change their sizes, optical and hygroscopic properties as

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well as lifetime in the atmosphere

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

14) Page 11580, line 19, enhances hygroscopic properties and original particles

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

16) Page 11580, line 22, little attention has

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

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

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

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

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

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

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

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

25) Page 11583, line 4, before a sample

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

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

28) Page 11583, line 16-17, A single-beam spectrum collected prior to the SO<sub>2</sub> exposure was used as the reference spectrum

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.

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- 30) Page 11583, line 19, SO<sub>2</sub> have a
- 31) Page 11585, line 6-7, A blank analysis was performed prior to running a sample analysis
- 32) Page 11585, line 18, delete 'as can be seen in Fig. 1a.'
- 33) Page 11585, line 21, assigned to adsorbed bisulfate
- 34) Page 11586, line 6-7, The peak at 1335 cm<sup>-1</sup>
- 35) Page 11586, line 10, peak fitting using a combination of
- 36) Page 11586, line 12, 1158 cm<sup>-1</sup> simultaneously increase
- 37) Page 11586, line 15, and then slightly decreases in intensity
- 38) Page 11586, line 18, bisulfate and sulfate adsorbed on
- 39) Page 11586, line 19, spell out 'PDF-TIR'
- 40) Page 11586, line 22, after drying of a hematite layer
- 41) Page 11586, line 24 He suggested that the conversion
- 42) Page 11586, line 28, sulfate changed from
- 43) Page 11586, line 29, on {012} and {1m0} surfaces
- 44) Page 11587, line 1, and they suggested
- 45) Page 11587, line 3, delete "obviously". Please delete most "obviously" and "clearly" in the paper. They are redundant words.
- 46) Page 11587, line 4, remains controversial
- 47) Page 11587, line 15, along with consumption of
- 48) Page 11587, line 24, in this region because of the increase of

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- 49) Page 11587, line 26, HSO<sub>3</sub>- and SO<sub>3</sub><sup>2-</sup>. Same applied to page 11595, line 12; page 11597, line 11; page 11601, line 16; page 11602, line 13
- 50) Page 11588, line 1, shows typical spectra
- 51) Page 11588, line 2, delete 'In Fig. 1b, '
- 52) Page 11588, line 4-5 be assigned to surface-coordinated
- 53) Page 11588, line 15, delete 'compared with that of hematite,'
- 54) Page 11588, line 17, delete 'as the reaction proceeds,'
- 55) Page 11588, line 23-24, is composed of three major peaks at 1027, 1155 and 1094 cm<sup>-1</sup>.
- 56) Page 11589, line 6, are further oxidized in
- 57) Page 11589, line 11-12, should specify 'the same experiment'. Experiment with pure hematite or FN-24?
- 58) Page 11589, line 12, Figure 3 shows DRIFTS
- 59) Page 11589, line 13, delete 'increasing'
- 60) Page 11589, line 14, delete 'in the same experiment. As shown in Fig. 3. '
- 61) Page 11590, line 2, delete 'product'
- 62) Page 11590, line 4, at 1716, 1697, 1686 and 1676 cm<sup>-1</sup>
- 63) Page 11590, line 8-9, reverse the listing order as well
- 64) Page 11590, line 10-11, This result confirms that adsorbed HNO<sub>3</sub>
- 65) Page 11590, line 12, The formation of HNO<sub>3</sub>-H<sub>2</sub>O complexes
- 66) Page 11590, line 14-15, no gas phase HNO<sub>3</sub> was observed in White cell-FTIR experiments as discuss later.

- 67) Page 11590, line 15-16, molecularly adsorbed nitric acid.
- 68) Page 11590, line 17, in previous reports
- 69) Page 11590, line 26, compared to previous studies
- 70) Page 11590, line 27-29, rephrase 'which may suggest. ...interactions with H<sub>2</sub>O'. 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<sub>2</sub>O present. This is consistent with the fact that no gas phase N<sub>2</sub>O<sub>4</sub> was detected in Whole cell-FTIR experiments as discussed later.
- 72) Page 11591, line 12, are stretching vibration modes of isolated surface
- 73) Page 11591, line 13, ions of octahedral sites and tetrahedral sites
- 74) Page 11591, line 14, that surface OH groups
- 75) Page 11591, line 15, are reaction active sites
- 76) Page 11591, line 17, slowly increases in intensity
- 77) Page 11591, line 21, surface-adsorbed HNO<sub>3</sub> discussed earlier.
- 78) Page 11591, line 22, delete 'mentioned above clearly'
- 79) Page 11592, line 3-4, All of the DRIFTS experiments
- 80) Page 11592, line 13, of different reaction product
- 81) Page 11592, line 14, one another, the peaks were deconvoluted before integration in some experiments.
- 82) Page 11592, line 16, since O<sub>2</sub> was in great excess compared to SO<sub>2</sub>
- 83) Page 11593, line 4, delete 'as shown in Fig. 4.'
- 84) Page 11593, line 10, delete 'under the same reaction conditions'

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- 85) Page 11593, line 13-14, the reaction behavior of SO<sub>2</sub> adsorbed on hematite
- 86) Page 11593, line 15, should receive close attention
- 87) Page 11593, line 16, in ambient particles
- 88) Page 11593, line 19, and possible gaseous
- 89) Page 11593, line 22, from exposure of the FN-24 sample
- 90) Page 11594, line 1-2, but different rates of SO<sub>2</sub> consumption
- 91) Page 11594, line 5, and the FN-24 sample
- 92) Page 11594, line 6, with the rate of sulfate formation observed in DRIFTS experiments.
- 93) Page 11594, line 10, to lower concentrations of SO<sub>2</sub>.
- 94) Page 11594, line 11, although adsorbed HNO<sub>3</sub>
- 95) Page 11594, line 13, observed in White cell-FTIR
- 96) Page 11594, line 15, from exposure of the FN-90 sample
- 97) Page 11594, line 16, was obtained
- 98) Page 11594, line 25, the degradation of primary
- 99) Page 11595, line 4, delete 'detectable'. Same applied to line 8-9
- 100) Page 11595, line 5, It is possible that gaseous NO
- 101) Page 11595, line 14-18, split into two sentences. 'many more reduced' change to 'much more reduced', 'longer' change to 'long'
- 102) Page 11595, line 25, surface of FN samples placed in the White cell.'
- 103) Page 11596, line 1, White cell-FTIR and DRIFTS techniques

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- 104) Page 11596, line 2, show no detectable gas phase products, indicating
- 105) Page 11596, line 20, the contribution of HONO by this
- 106) Page 11596, line 25, mixtures at both low and high SO<sub>2</sub>
- 107) Page 11596, line 26, delete 'gradually'
- 108) Page 11597, line 25, at room temperature
- 109) Page 11598, line 1, 'strong acidity' is vague, should at least provide a range of pH
- 110) Page 11599, line 1-2, shows SEM images
- 111) Page 11599, line 5-6, delete 'After comparing these images, we notice that'
- 112) Page 11600, line 12, on hematite-nitrate mixtures
- 113) Page 11603, line 3, strongly with water and adsorbed HNO<sub>3</sub>
- 114) Page 11603, line 6, This can explain small amounts of
- 115) Page 11603, line 25, delete 'at last'
- 116) Page 11603, line 26, during heterogeneous hydrolysis
- 117) Page 11604, line 24, delete 'Compared with hematite solely, '
- 118) Page 11605, line 2, on particle surfaces and
- 119) Page 11605, line 23, change comma to period
- 120) Page 11615, Fig. 2 caption, Peak fitting of the
- 121) Page 11618, Fig. 5 caption, delete space between 21 and %. Same applied to Fig. 6 and 7

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 11577, 2014.

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