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Atmospheric Chemistry and Physics Discussions

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

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This paper investigates the effect of nitrate on the heterogeneous conversion of SO2 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 SO2 oxidation to sulfate on hematite surface. The nitrate itself can convert into surface adsorbed HNO3 and N2O4 as well as gas phase N2O and HONO. The findings reveal a new SO2 oxidation pathway as well as a potential source of N2O 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.

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.

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?

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 SO2 only reaches the surface) and the BET surface area of the sample (assuming SO2 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 N2O 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.

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-1). 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, line5, 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

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 hydroscopic 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 revel 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 place into the ceramic sample holder

25) Page 11583, line 4, before a ample

26) Page 11583, line 5, A 30-mg sample was place 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 SO2 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.

30) Page 11583, line 19, SO2 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-1

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

36) Page 11586, line 12, 1158 cm-1 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 ‘PDFTIR’

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

49) Page 11587, line 26, HSO3- and SO32-. 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, lien 23-24, is composed of three major peaks at 1027, 1155 and 1094 cm-1.

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-1

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

64) Page 11590, line 10-11, This result confirms that adsorbed HNO3

65) Page 11590, line 12, The formation of HNO3-H2O complexes

66) Page 11590, line 14-15, no gas phase HNO3 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 H2O'. change 'is interacting with' to 'interacts with'. Either delete 'may' or 'perhaps'

71) Page 11591, line 1-3, particle surface with nitric acid and H2O present. This is consistent with the face that no gas phase N2O4 was detected in While cell-FTIR experiments as discuss 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 HNO3 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 O2 was in great excess compared to SO2

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 SO2 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 SO2 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 SO2.

94) Page 11594, line 11, although adsorbed HNO3

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

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 SO2

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 HNO3

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

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