

Answer to the referees comments

Anonymous Referee #2

We thank reviewer #2 for these helpful comments and have made a lot revision about the manuscript following the suggestion.

This paper used SEM-EDX, TPD and FTIR to study morphology, elements and chemical compositions of Asian dust particles collected in Beijing, used Knudsen cell measured the initial uptake coefficient of SO₂ on the particles, and used infrared absorption peak of water to discuss the hygroscopic property of dust particles and the particles reacted with SO₂, it concludes that SO₂ has low reactivity on the Asian dust particles, both under wet and dry conditions. This study provides new information for the Asian dust, however, I have a number of concerns about the methodology and the discussion.

Response: We appreciate very much for the positive comments.

1. In the introduction section, it seems that the authors are not familiar with the reported researches in this field, it says "Little data is available, however, on the heterogeneous reactivity and hygroscopic behavior of the Asian dust particles"(Pg 8901 line 26-27). In fact, many field and laboratory studies have been conducted on the heterogeneous reactivity and hygroscopic properties of Asian dust and its main components. (Hanisch and Crowley, 2000; Underwood et al., 2001;Laskin et al., 2005;Ullerstam et al., 2003; Zhang et al., 2006; Sullivan et al., 2009), which the authors did not mention. Similarly, for the laboratory studies on SO₂ reaction on mineral dust (Ullerstam et al., 2002; Ullerstam et al., 2003; Li et al., 2006; Zhang et al., 2006; Prince et al., 2007), the author only mentioned one model study (P8902 Line3-5 "Numerous field, laboratory and modeling studies have provided convincing evidence that mineral dust plays an important role in the chemistry of sulfur dioxide (Dentener et al., 1996; Song and Carmichael, 1999)."

Response: We thank the reviewer to bring these reported researches to our attention. The following sentences are added. "Since the information about the heterogeneous reactivity and hygroscopic properties is crucial in predicting mineral dust impacts on climate and atmospheric environment, many field and laboratory studies have been conducted on mineral dust and its main components (Hanisch and Crowley, 2000; Koehler et al, 2009; Laskin et al., 2005b; Maxwell-Meier et al. 2004; Shi et al, 2008; Sullivan et al., 2009; Ullerstam et al., 2003; Underwood et al., 2001; Zhang et al., 2006)." The reported studies on SO₂ reaction on mineral dust are also added.

2. The authors need to address if the Asian dust is unique compared to other dusts in the sense of chemical compositions, otherwise, it is no need to separate Asian dust from other mineral dusts. Dust particles from different regions have similar major components, such as aluminosilicate, carbonate, and oxides; while their fractions may be vary. It makes more sense to know the compositions of the dust particles, before carrying out laboratory study on the physicochemical properties of the dust particles.

Response: We appreciate very much for the constructive suggestion. It is true dust particles from different regions have similar major components, such as aluminosilicate, carbonate, and oxides; while their fractions may be vary. Compared to pure substitutes of mineral dust, authentic dust always mixed with various species which possible alter the reactivity. In fact, the composition

analysis was for interpreting the heterogeneous reaction experimental results in this study.

3. Pg8902 line 8-9, from just one observation (Xie et al 2005), the author came to the conclusion that the conversion rate of SO₂ to sulfate is low, many observation studies on the composition, concentration, and properties of dust particles were not mentioned in the paper. For example, the internal mixing of sulfate and aluminosilicate observed during ACE-Asia (Sullivan et al., 2007), and the study on the interaction between sulfate and mineral dust (Arimoto et al., 2006; Tang et al., 2004; Jordan et al., 2003).

Response: We thank the reviewer to bring these reported researches to our attention. Some related references and the following sentences are added. "Several observation-based studies have reported that although East Asian dust particles have long contact times with sulfate and nitrate precursors, they contain only small amounts (typically, less than 10-50%) of sulfate and nitrate (Maxwell-Meier et al. 2004; Ro et al. 2005; Zhang, D. Z., and Iwasaka, Y., 1999;)." "The unexpected low amount of sulfur species disagrees with some previous researches where sulfur species were always detected in Asian dust storm particles (Ro et al., 2005; Shi et al., 2008; Song and Carmichael, 1999; Sullivan et al., 2007a; Zhang and Iwasaka, 1999). However, EDX analysis of individual dust storm particle also implied that almost no sulfate is formed on the surface of dust storm particles during their transport from source areas to Beijing (Zhang and Iwasaka, 1999). In addition, it was reported that more than 90% of Asian Dust particles collected in Qingdao, China during three Asian Dust events in the spring of 2001 were not disturbed by sulfate, nitrate, and/or sea-salts (Zhang et al., 2000). It seems the dust storm particle has low reactivity to SO₂ since SO₂ emissions are high in China."

4. The dust particle sampling method of the study is not representing the particles in the atmosphere. The authors used a "clean jar" to collect one dust event in April 2006 (Pg 8902 line 21-23) for the study. No information about the sampling method, number of samples, and size distribution of the dust particles was provided. Sample from one event at a specific event could not represent the Asian dust, not to mention that the sample collected was those deposited on the ground, which are generally coarse particles, this is why they got large size ($d_{0.5}=20 \mu\text{m}$). Comparing to coarse particles, fine particles could have very different compositions, surface area/volume ratio, and reactivity; this might be the reason why they observed low sulfur content. The composition, concentration, and properties of dust particles are influenced by sources, transport paths, and interaction with gaseous pollutants, studies on the SO₂ reaction with Asian dust from samples of just one dust event should not be extrapolated to the whole Asian dust.

Response: It is not a traditional particle collection method for particles characterization. However, the particles collected by this way also represent dust particles and it provided an effective way to collect enough particles for laboratory reaction study since the major focus in this study was the reactivity of authentic Asian dust particles to SO₂.

Nevertheless, it is not suitable to extrapolate the results to the whole Asian dust. And the sentence "These results indicate that the impact of dust storm on atmospheric SO₂ removal should not be overestimated." is removed. The title of this paper is also changed to "A case study of Asian dust storm particles: chemical composition, reactivity to SO₂, and the hygroscopic property".

5. Usually SEM-EDX analysis is based on analyzing a large number of particles collected with single particle sampler. The authors only used Figure 1 (SEM-EDX measurement) to illustrate the compositions of dust particles, and provided no information about the number of particles

measured and the size distribution; one may doubt its representativeness. The SEM-EDX analysis was conducted by depositing particles on copper after dispersed in water (Pg 8902 line 5-8), with this process, water soluble components, such as $\text{Ca}(\text{NO}_3)_2$, $(\text{NH})_4\text{SO}_4$, CaSO_4 could be lost, hence the results could not reflect the original dust particles.

Response: The preparation way from SEM/EDX analysis may be not suitable because the soluble components were destroyed. Therefore, XPS analysis results which showed similar results as EDX with high fraction of C and no detection of S were added in revised manuscript. EDX and XPS results provided complementary information of surface species on particles.

6. The authors used Mg/Al ratios of soil from different regions and concluded that “The results do imply, however, that other aerosol sources are continually deposited on the dust particles during transportation.”(P8905 line 28-P8906 line 1). It did not give the source of air mass; thus it is hard to know what “Other aerosol source” means.

Response: It is an incorrect description and it is changed to “other components are continually deposited on the dust particles during transportation.”

7. P8906 line15-24, P8907 line 26-28, the bulk sample used by the authors could not separate external and internal mixing states; the observation of NO production should not be used as a direct evidence of NO_3^- coating.

Response: Since individual particles analysis was not conducted, the mixture state assumed was not suitable in this study. The sentence was removed. “These processes resulted in the nitrate coated on dust.”

8. Figure 5b, with AFM Krueger et al (Krueger et al., 2005) have showed that water is not evenly distributed on the surface, it is more proper to use the integrated absorption area of water to discuss the role of RH.

Response: For DRIFTS study, K-M function is usually used for the quantitative description of surface species. Therefore, K-M was used to quantify the role of RH.

9. Pg 8912 line 5, in Al-Hosney et al., 2005, no oxidization of SO_2 by HNO_3 was mentioned, delete this.

Response: It has been deleted.

10. Pg 8912 line 19-20, the statement “These results suggest that the removal effect of SO_2 by mineral dust during dust storms should not be overestimated.” is not correct. Besides uptake by mineral dust, SO_2 could also be oxidized by O_3 on the surface of mineral dust particles (Li et al, 2006).

Response: The statement has been removed.

- Arimoto, R., Kim, Y. J., Kim, Y. P., Quinn, P. K., Bates, T. S., Anderson, T. L., Gong, S., Uno, I., Chin, M., Huebert, B. J., Clarke, A. D., Shinozuka, Y., Weber, R. J., Anderson, J. R., Guazzotti, S. A., Sullivan, R. C., Sodeman, D. A., Prather, K. A., and Sokolik, I. N.: Characterization of Asian Dust during ACE-Asia, *Global and Planetary Change*, 52, 23-56, 10.1016/j.gloplacha.2006.02.013, 2006.
- Hanisch, F., and Crowley, J. N.: The heterogeneous reactivity of gaseous nitric acid on authentic mineral dust samples, and on individual mineral and clay mineral components, *International Discussion Meeting of the Deutsche-Bunsen-Gesellschaft-fur-Physikalische-Chemie*, Gottingen, Germany, 2000, ISI:000169504900039, 2474-2482,
- Jordan, C. E., Dibb, J. E., Anderson, B. E., and Fuelberg, H. E.: Uptake of nitrate and sulfate on dust aerosols during TRACE-P, *J. Geophys. Res.-Atmos.*, 108, 1-10, 8817 , 10.1029/2002jd003101, 2003.
- Krueger, B. J., Ross, J. L., and Grassian, V. H.: Formation of microcrystals, micropuddles, and other spatial inhomogenities in surface reactions under ambient conditions: An atomic force microscopy study of water and nitric acid adsorption on MgO(100) and CaCO₃(1014), *Langmuir*, 21, 8793-8801, 2005.
- Laskin, A., Wietsma, T. W., Krueger, B. J., and Grassian, V. H.: Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCSEM/EDX, ESEM, and ICP-MS study, *J. Geophys. Res.-Atmos.*, 110, 15, D10208 Artm d10208, 2005.
- Li, L., Chen, Z. M., Zhang, Y. H., Zhu, T., Li, J. L., and Ding, J.: Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate, *Atmospheric Chemistry and Physics*, 6, 2453-2464, 2006.
- Prince, A. P., Kleiber, P., Grassian, V. H., and Young, M. A.: Heterogeneous interactions of calcite aerosol with sulfur dioxide and sulfur dioxide-nitric acid mixtures, *Physical Chemistry Chemical Physics*, 9, 3432-3439, 10.1039/b703296j, 2007.
- Sullivan, R. C., Guazzotti, S. A., Sodeman, D. A., and Prather, K. A.: Direct observations of the atmospheric processing of Asian mineral dust, *Atmos. Chem. Phys.*, 7, 1213-1236, 2007.
- Sullivan, R. C., Moore, M. J. K., Petters, M. D., Kreidenweis, S. M., Roberts, G. C., and Prather, K. A.: Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles, *Atmospheric Chemistry and Physics*, 9, 3303-3316, 2009.
- Tang, Y. H., Carmichael, G. R., Kurata, G., Uno, I., Weber, R. J., Song, C. H., Guttikunda, S. K., Woo, J. H., Streets, D. G., Wei, C., Clarke, A. D., Huebert, B., and Anderson, T. L.: Impacts of dust on regional tropospheric chemistry during the ACEAsia experiment: A model study with observations, *J. Geophys. Res.-Atmos.*, 109, D19s21 10.1029/2003jd003806, 2004.
- Ullerstam, M., Vogt, R., Langer, S., and Ljungstrom, E.: The kinetics and mechanism of SO₂ oxidation by O₃ on mineral dust, *Physical Chemistry Chemical Physics*, 4, 4694-4699, 10.1039/b203529b, 2002.
- Ullerstam, M., Johnson, M. S., Vogt, R., and Ljungstrom, E.: DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO₂ and NO₂ on mineral dust, *Atmospheric Chemistry and Physics*, 3, 2043-2051, 2003.
- Underwood, G. M., Song, C. H., Phadnis, M., Carmichael, G. R., and Grassian, V. H.: Heterogeneous reactions of NO₂ and HNO₃ on oxides and mineral dust: A combined laboratory and modeling study, *Journal of Geophysical Research-Atmospheres*, 106, 18055-18066, 2001.
- Zhang, X. Y., Zhuang, G. S., Chen, J. M., Wang, Y., Wang, X., An, Z. S., and Zhang, P.: Heterogeneous reactions of sulfur dioxide on typical mineral particles, *Journal of Physical Chemistry B*, 110, 12588-12596, 10.1021/jp0617773, 2006.

Response: Thanks for the valuable recommendations. The related references were added.