



Laboratory simulation of SO₂ heterogeneous reactions on hematite surface under different SO₂ concentrations

CUI Huxiong¹, CHENG Tiantao^{1,3,*}, YU Xingna², CHEN Jianmin¹,
XU Yongfu³, FANG Wen⁴

1. Center for Atmospheric Chemistry Study, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China. E-mail: 072047010@fudan.edu.cn

2. Key Laboratory for Atmospheric Physics and Environment, Nanjing University of Information Science and Technology, Nanjing 210044, China

3. State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Science, Beijing 100029, China

4. Institute of Weather Modification, Chinese Academy of Meteorological Sciences, Beijing 100084, China

Received 18 September 2008; revised 26 October 2008; accepted 20 November 2008

Abstract

The variations of sulfate formation and optical coefficients during SO₂ heterogeneous reactions on hematite surface under different SO₂ concentrations were examined using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and ion chromatograph (IC). Laboratory experiments revealed that within ambient SO₂ of 0.51–18.6 ppmv, sulfate product, producing velocity, absorption and backward scattering coefficients showed an increasing trend with SO₂ concentration. Under given SO₂ concentration, the velocity of sulfate producing performed an evolution of initial increasing, midterm decreasing and final stabilizing. The reactive uptake and Brunauer-Emmett-Teller (BET) uptake coefficients of heterogeneous reactions rose with SO₂ and exhibited high reactivities. Considering global warming, this result is important for the knowledge of heterogeneous reactions of SO₂ on mineral particle surface in the atmosphere and the assessment of their impacts on radiative forcing.

Key words: hematite; heterogeneous reaction; sulfate; optical coefficient

DOI: 10.1016/S1001-0742(08)62388-8

Introduction

Arid area accounts for about 33% of the earth's land, which is one potential origin of atmospheric aerosols. Mineral aerosol as a major contributor is estimated to be about 1/2 of the tropospheric aerosol budget, with the annual amount of 1000–3000 Tg (Dentener *et al.*, 1996). Mineral aerosol always contains so many metal elements and corresponding oxides existed in the earth crust, such as CaCO₃, CaO, Al₂O₃, and so on. Except for SiO₂ and Al₂O₃, iron is a major element (3.089%) and Fe₂O₃ is the most important oxide (about 6.28%) which can accelerate the velocity of SO₂ converting to sulfate within mineral aerosol (Usher *et al.*, 2003). SO₂ is one of most important gaseous pollutants and precursors to cause sulfate and acid rain. In the atmosphere, SO₂ can be converted into H₂SO₄ and then sulfate through gas-to-particle process on the surface of cloud droplet or liquid particle, and form secondary aerosol through its heterogeneous reaction with preexistent particle (Zhang *et al.*, 2006b; Urone *et al.*, 1968; Hug, 1997; Judeikis *et al.*, 1978). Sulfate is one of most important atmospheric aerosols impacting the climate

system through not only absorbing and scattering solar radiation, but also acting as cloud condensation nuclei (CCN) to influence the optical property and lifetime of clouds.

Although much attention was paid to atmospheric heterogeneous reactions (Ding and Zhu, 2003; Gao and Chen, 2006; Goodman *et al.*, 2001; Halstead *et al.*, 1990; Hoffmann *et al.*, 1996; Jang and Kamens, 2001; Mogili *et al.*, 2006), up to now, the heterogeneous reaction of SO₂ on mineral particle surface has not been understood completely. Ullerstam *et al.* (2002) used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to study the mechanism and kinetics of SO₂ reactions on mineral particle surface. Fu *et al.* (2007) presented the heterogeneous uptake and oxidation of SO₂ on iron oxides. However, the knowledge of sulfate formation and optical property variance related to SO₂ heterogeneous reactions with mineral aerosol is extremely limited.

In order to better understand how chemical reactions affect the optical property of aging mineral aerosols transported over downwind industrial regions, it is needed to simulate the heterogeneous reaction of SO₂ on the surface of iron oxidants representing the real mineral particles (Hematite) in laboratory facility. In this article,

* Corresponding author. E-mail: ttcheng@fudan.edu.cn

jesoc.ac.cn

SO₂ heterogeneous reactions with α -Fe₂O₃ under different concentrations, as well as their effects on the sulfate production and particle optical property were investigated using in situ DRIFTS and ion chromatograph (IC).

1 Experiments

1.1 Materials

α -Fe₂O₃ was synthesized according to the method by Schwertmann and Cornell (2000). The purity of SO₂ standard gas reaches 99.99%. Ar and O₂ were pure of over 99.999% (Shanghai Yunguang Industrial Gas Company Ltd., China).

1.2 Apparatus

DRIFTS was used to simulate particulate surface chemical reactions. During chemical experiments, the reagent of powdered α -Fe₂O₃ sample was placed in a ceramic crucible in the chamber of spectra-tech diffuse reflectance accessory. Infrared spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer (Thermo Electron Corporation, USA), and a spectra-tech diffuse reflectance accessory was equipped with liquid-nitrogen cooled mercury cadmium telluride (MCT) detector (Thermo Electron Corporation, USA). FT-IR spectral range is in 4000–600 cm⁻¹, resolution 4 cm⁻¹ and scanning 64 times for each spectrum. Then, the spectra were analyzed qualitatively and quantitatively using OMNIC software (version 7.2a). IC (Dionex Corporation, USA) with a AS14 anion exchange resin column was used to quantify sulfate product, in which mobile phase was one mixture of sodium carbonate (3.7 mol/L) and sodium bicarbonate (1.0 mol/L), with an airflow rate of 1.5 mL/min.

1.3 Methods

The detailed schematic diagram of DRIFTS was described previously by Wang *et al.* (2001) and Zhang *et al.* (2006b). In each experiment, one particle sample of 30 mg in 2.16 mm thickness was usually placed on the holder of DRIFTS reaction chamber. Before introducing reaction gas, Ar was introduced into the chamber (123 mL/min) to blow off inside air and H₂O, and then Ar was used as the carrier gas to load mixture of standard SO₂ and O₂ into the reactor. The airflow velocity of Ar in pipe was 94.8 mL/min, and O₂ was 26.2 mL/min.

1.4 Calculation

1.4.1 Optical coefficients

The extinction coefficient (σ_e) is defined with Beer-Lambert's law as Eq. (1).

$$I = I_0 e^{-\sigma_e x} \quad (1)$$

where, I_0 is the intensity of initial light, I is the remaining light intensity after passing through a medium with thickness x .

The Kubelka-Munk (KM) theory (Kubelka, 1948;

Kubelka and Munk, 1931) is defined as Eq. (2).

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \quad (2)$$

where, R_∞ is the reflectance of sample relative to that of an appropriate reference material, when both sample and reference satisfy the "infinite depth" criterion. K and S are the absorption and backward scattering coefficients, respectively.

1.4.2 Sulfate product

The adsorption band between 1300 and 1100 cm⁻¹, centered on operating wavelength of 0.87 μ m, can feature SO₄²⁻ formation and characterize sulfate production (Ullerstam *et al.*, 2002). IC was firstly used to quantify the sulfate product of several reactive times. Then, these IC quantified sulfate products versus corresponding peak areas of DRIFTS infrared spectra were plotted and fitted linearly. Based on this linear relationship, the amount of sulfate formed at other reactive times can be determined.

1.4.3 Reaction kinetics coefficients

The reactive uptake coefficient (γ_{obs}) is defined as the velocity of sulfate formation on surface ($dC_{\text{SO}_4^{2-}}/dt$) divided by the total number of surface collisions per unit time (Z) (Ullerstam *et al.*, 2003).

$$\gamma_{\text{obs}} = \frac{dC_{\text{SO}_4^{2-}}/dt}{Z} \quad (3)$$

$$Z = \frac{1}{4} A_s C_{\text{SO}_2} v_{\text{SO}_2} \quad (4)$$

where, v_{SO_2} is the mean molecular velocity of SO₂ calculated as $\sqrt{8RT/\pi M_{\text{SO}_2}}$, A_s is the reactive surface area (0.785 cm²), and C_{SO_2} is SO₂ concentration.

The Brunauer-Emmett-Teller (BET) uptake coefficient (γ_{BET}) was deduced from Eq. (4).

$$\gamma_{\text{BET}} = \frac{\gamma_{\text{obs}} A_s}{A_{\text{BET}}} \quad (5)$$

where, A_{BET} (m²/g) is the BET surface area measured by ASAP 2010.

2 Results and discussion

According to mean SO₂ concentration, the daily air quality was defined as unpolluted (< 0.053 ppmv), light pollution (0.053–0.28 ppmv), moderate pollution (0.28–0.56 ppmv) and heavy pollution (> 0.56 ppmv) by the Environment Protection Community in China. SO₂ is harmful for people's respiratory tract once its concentration exceeds 1.0 ppmv. However, in the appearance of particles, SO₂ can cause a larger damage to human body than its individual even less 1.0 ppmv. In industrial regions, large amounts of no-diffused SO₂ always result in serious smog affair, e.g., Belgian Muse canyon smog in Dec. 1930 (9.0–38.0 ppmv), U.S.A. Donora smog in

Oct. 1948 (0.5–2.0 ppmv), and renowned London smog in Dec. 1952. Consistent with the SO₂ levels used previously in experiments (Scaringelli *et al.*, 1967; Chun and Quon, 1973), the SO₂ range 0.51–18.6 ppmv was selected for heterogeneous reactions.

2.1 Absorption and backward scattering coefficients

Figure 1 shows the series of absorption and backward scattering coefficients at the wavelength of 8.7 μm in the heterogeneous reactions of SO₂ on α-Fe₂O₃ particulate surface under different SO₂ concentrations (0.51, 2.41, 4.85, 10.02 and 18.6 ppmv). The absorption and backward scattering coefficients showed an increasing trend with either reaction time or SO₂ concentration. The absorption coefficient reached maximums (3321, 4942, 6380, 7930, 10249 km⁻¹ for above five SO₂ levels, respectively) at 120 min. The backward scattering coefficients were up to 25525, 36828, 41896, 46610, 74374 km⁻¹, respectively at 30 min, which were about 37%–78% of those at 120 min. Compared with other periods of reactions, the absorption and backward scattering coefficients, and the velocity of sulfate producing rose up dramatically during early period (30 min). This revealed that the early reaction

period played a key role in the experiment. Moreover, the absorption and backward scattering coefficients of these experiments fell in a magnitude same with previous observations obtained in the atmosphere (Andreae *et al.*, 2008; Lyamani *et al.*, 2007; Meszaros *et al.*, 1998; Slater *et al.*, 2002).

2.2 Sulfate production

SO₂ concentration is an important factor to control the heterogeneous reaction of SO₂ with α-Fe₂O₃. As shown in Fig. 2a, at 120 min, the amount of sulfate ongoing production increased to 0.48, 0.78, 0.95, 1.02 and 1.17 mg/L in the five target experiments, respectively. Chun and Quon (1973) measured the sulfate of 260 to 351 μg formed on the surface of ferric oxide particles per 5 mg, and Zhang *et al.* (2006a) reported the amount of sulfate formation about 50 μg/mg for Fe₂O₃. Due to different conditions in control reactions, these previous results are larger than current experiments.

As shown in Fig. 2b, the velocity of SO₄²⁻ producing behaved itself with a pattern of initial increasing, next decreasing and final stabilizing during the whole reaction period. In particular, with the increase of SO₂ concen-

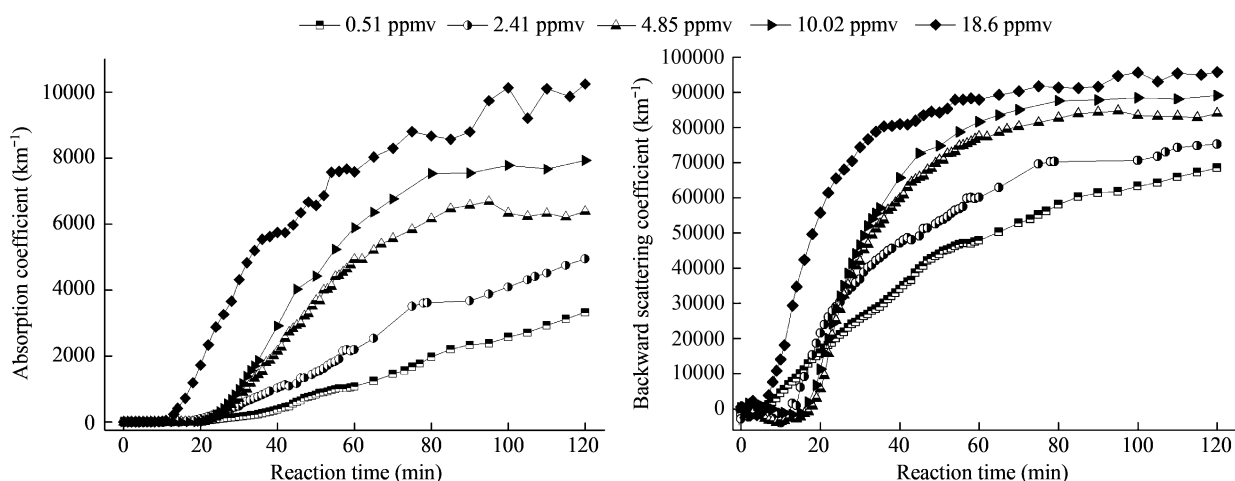


Fig. 1 Absorption and backward scattering coefficients at the wavelength of 8.7 μm in the heterogeneous reactions of different SO₂ concentrations.

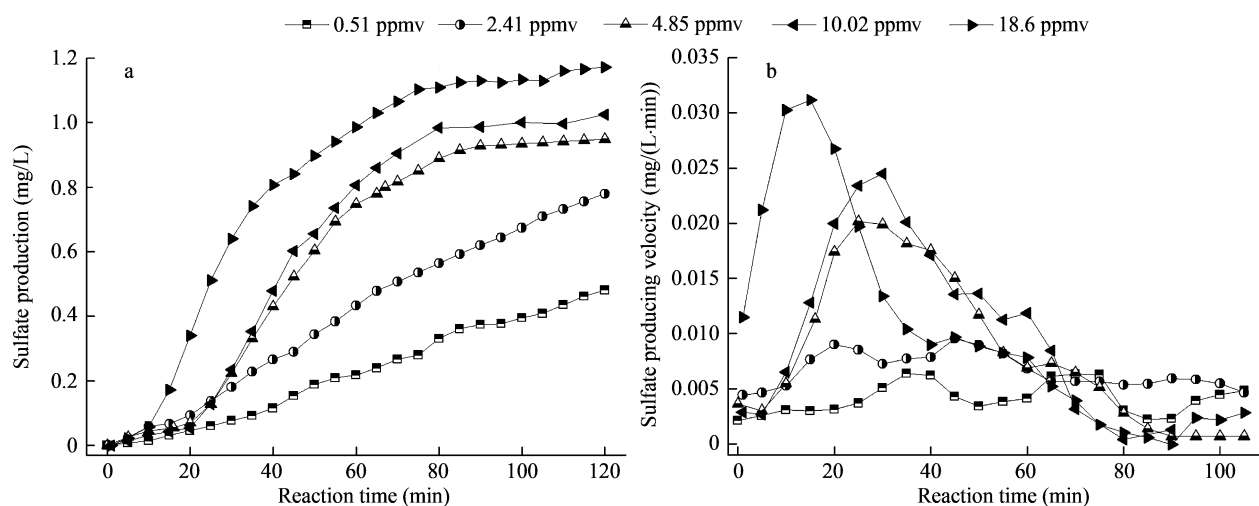


Fig. 2 Sulfate production (a) and producing velocity (b) in heterogeneous reactions under different SO₂ conditions.

tration, the time for SO_4^{2-} producing velocity reaching maximum became shorter. Taking the experiment of SO_2 in 10.02 ppmv for example, the SO_4^{2-} producing velocity averaged for 5 min climbed up quickly to 0.013 mg/(L·min) during the early stage (0–30 min), reduced to 0.012 mg/(L·min) during the middle stage (30–70 min), and 0.001 mg/(L·min) during the late stage (70–120 min).

Theoretically, the SO_4^{2-} formation should infinitely quicken with the increase of SO_2 concentration and keep steady under one SO_2 constant concentration. But, in real reactions, the velocity of SO_4^{2-} producing increased initially and followed by the decrease. As the heterogeneous reaction proceeds at the isolated reactive sites which are scattered on the surface of metal oxidants, and the formed sulfate can be absorbed intensely and combined with iron oxides (Ullerstam *et al.*, 2003; Fu *et al.*, 2007), the reactive sites relative to heterogeneous reaction decrease dramatically and then directly reduce the velocity of SO_4^{2-} producing.

In order to further certify the impact of SO_2 concentration on SO_4^{2-} formation, two reaction kinetics factors of reactive uptake coefficient (γ_{obs}) and BET uptake coefficient (γ_{BET}) for SO_2 heterogeneous reaction with Fe_2O_3 were calculated (Table 1). Under constant O_2 concentration and temperature, the factors of γ_{obs} and γ_{BET} were contingent on SO_2 concentration and exhibited a high reactivity. This also approve that SO_2 concentration plays a key role in the whole heterogeneous reaction. Börensen *et al.* (2000) analyzed the γ_{obs} variation of NO_2 heterogeneous reaction on Alumina surface and described similar effects of NO_2 .

Table 1 Comparison of reactive uptake coefficient (γ_{obs}) and BET uptake coefficient (γ_{BET}) with the variation of SO_2 concentration in the presence of O_2 (5.65×10^{18} molecular/ cm^3), 298 K

C_{SO_2} (molecular/ cm^3)	γ_{obs}	γ_{BET}
2.69×10^{13}	4.4×10^{-5}	2.9×10^{-9}
6.48×10^{13}	5.8×10^{-5}	3.8×10^{-9}
2.69×10^{14}	1.5×10^{-4}	9.7×10^{-9}
5.00×10^{14}	2.3×10^{-4}	1.5×10^{-8}

3 Conclusions

For the heterogeneous reaction of SO_2 with $\alpha\text{-Fe}_2\text{O}_3$ representative of hematite aerosols, the changes of sulfate product and optical coefficient under different SO_2 conditions were examined using *in situ* DRIFTS and IC. Simulations reveal that SO_2 concentration has an important impact on all experiments of target heterogeneous reaction. The increase of sulfate production, producing velocity, absorption coefficient and backward scattering coefficient all are dependent on SO_2 concentration. In comparison with mid and late reaction periods, the early reaction process played a key role. The factors of reactive uptake coefficient (γ_{obs}) and BET uptake coefficient (γ_{BET}) are contingent on SO_2 concentration and exhibited a high reactivity. These results provide very important information for better understanding the impact of heterogeneous reaction of SO_2 on mineral aerosol to global warming.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 40533017, 20377008, 40605001), the National Key Technology R&D Program (No. 2006BAC12B001), and the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC-KF-2006-05) of China.

References

- Andreae M O, Schmid O, Yang H, Chand D, Yu J Z, Zeng L M *et al.*, 2008. Optical properties and chemical composition of the atmospheric aerosol in urban Guangzhou, China. *Atmospheric Environment*, 42(25): 6335–6350.
- Börensen C, Kirchner U, Scheer V, Vogt R, Zellner R, 2000. Mechanism and kinetics of the reactions of NO_2 or HNO_3 with alumina as a mineral dust model compound. *Journal of Physical Chemistry A*, 104: 5036–5045.
- Chun K C, Quon J E, 1973. Capacity of ferric oxide particles to oxidize sulfur dioxide in air. *Environmental Science and Technology*, 7(6): 532–538.
- Dentener F J, Carmichael G R, Zhang Y, Lelieveld J, Crutzen P J, 1996. Role of mineral aerosol as radiative surface in the global troposphere. *Journal of Geophysical Research*, 101: 22869–22889.
- Ding J, Zhu T, 2003. Heterogeneous reactions on the surface of fine particles in the atmosphere. *Chinese Science Bulletin*, 48(21): 2267–2276.
- Fu H B, Wang X, Wu H B, Yin Y, Chen J M, 2007. Heterogeneous uptake and oxidation of SO_2 on iron oxides. *Journal of Physical Chemistry C*, 111: 6077–6085.
- Gao Y C, Chen D, 2006. Heterogeneous reactions of sulfur dioxide on dust. *Science in China Series B-Chemistry*, 49(3): 273–280.
- Goodman A L, Li P, Usher C R, Grassian V H, 2001. Heterogeneous uptake of sulfur dioxide on aluminum and magnesium oxide particles. *Journal of Physical Chemistry A*, 105: 6109–6120.
- Halstead J A, Armstrong R, Pohlman B, Sibley S, Maier R, 1990. Nonaqueous heterogeneous oxidation of sulfur dioxide. *Journal of Physical Chemistry*, 94: 3261–3265.
- Hoffmann P, Dedik A N, Enslin J, Weinbruch S, Weber S, Sinner T *et al.*, 1996. Speciation of iron in atmospheric aerosol samples. *Journal of Aerosol Science*, 27(2): 325–337.
- Hug S J, 1997. *In situ* Fourier transform infrared measurements of sulfate adsorption on hematite in aqueous solutions. *Journal of Colloid and Interface Science*, 188: 415–422.
- Jang M, Kamens R M, 2001. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environmental Science and Technology*, 35: 4758–4766.
- Judeikis H S, Stewart T B, Wren A G, 1978. Laboratory studies of heterogeneous reaction of SO_2 . *Atmospheric Environment*, 12: 1633–1641.
- Kubelka P, 1948. New contributions to the optics of intensely scattering materials. Part I. *Journal of the Optical Society America*, 38: 448–457.
- Kubelka P, Munk F, 1931. Ein Beitrag zur Optik der Farbanstriche. *Zeitschrift für technische Physik*, 12: 593–601.
- Lyamani H, Olmo F J, Arboledas L A, 2007. Light scattering and absorption properties of aerosol particles in the urban environment of Granada, Spain. *Atmospheric Environment*,

- 42(11): 2630–2642.
- Meszaros E, Molnar A, Ogren J, 1998. Scattering and absorption coefficients vs. chemical composition of fine atmospheric aerosol particles under regional condition in Hungary. *Journal of Aerosol Science*, 29(10): 1171–1178.
- Mogili P K, Kleiber P D, Young M A, Grassian V H, 2006. Heterogeneous uptake of ozone on reactive components of mineral dust aerosol: An environmental aerosol reaction chamber study. *Journal of Physical Chemistry A*, 110: 13799–13807.
- Scaringelli F P, Saltzman B E, Frey S A, 1967. Spectrophotometric determination of atmospheric sulfur dioxide. *Analytical Chemistry*, 39: 1709–1719.
- Schwertmann U, Cornell R M, 2000. Iron oxides in the laboratory: Preparation and characterization. New York: Wiley-VCH.
- Slater J F, Dibb J E, Keim B D, Talbot R W, 2002. Light extinction by fine atmospheric particles in the White Mountains region of New Hampshire and its relationship to air mass transport. *The Science of the Total Environment*, 287: 221–239.
- Ullerstam M, Johnson M S, Vogt R, Ljungström E, 2003. DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO₂ and NO₂ on mineral dust. *Atmospheric Chemistry and Physics*, 3: 2043.
- Ullerstam M, Vogt R, Langer S, Ljungström E, 2002. The kinetics and mechanism of SO₂ oxidation by O₃ on mineral dust. *Physical Chemistry Chemical Physics*, 4: 4694–4699.
- Urone P, Lutsep Helmut, Noyes C M, Parcher J F, 1968. Static studies of sulfur dioxide reactions in air. *Environmental Science and Technology*, 2(8): 611–618.
- Usher C R, Michel A E, Grassian V H, 2003. Reaction on mineral dust. *Chemical Reviews*, 103: 4883–4939.
- Wang L, Zhang F, Chen J M, 2001. Carbonyl sulfide derived from catalytic oxidation of carbon disulfide over atmospheric particles. *Environmental Science and Technology*, 35(12): 2543–2547.
- Zhang Q J, Wang X, Chen J M, Zhuang G S, 2006a. Formation of Fe(II) (aq) and sulfate via heterogeneous reaction of SO₂ with Fe₂O₃. *Chemical Journal of Chinese Universities*, 27(7): 1347–1350.
- Zhang X Y, Zhuang G S, Chen J M, Wang Y X, An Z S, Zhang P, 2006b. Heterogeneous reactions of sulfur dioxide on typical mineral particles. *Journal of Physical Chemistry B*, 110: 12588–12596.