

**Effects of
temperature on the
heterogeneous
oxidation of SO₂**

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**Effects of temperature on the
heterogeneous oxidation of sulfur dioxide
by ozone on calcium carbonate**

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The heterogeneous oxidations of sulfur dioxide by ozone on CaCO_3 were studied as a function of temperature (230 to 298 K) at ambient pressure. Oxidation reactions were followed in real time using diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) to obtain kinetics and mechanistic data. From the analysis of the spectral features, the formation of sulfate was identified on the surface in the presence of O_3 and SO_2 at different temperatures from 230 to 298 K. The results showed that the heterogeneous oxidations and the rate of sulfate formation were sensitive to temperature. An interesting stage-transition state was observed at temperatures range from 230 to 257 K, but it became ambiguous gradually above 257 K. The reactive uptake coefficients at different temperatures from 230 to 298 K were acquired for the first time, which can be used directly in the model studies to predict the formation of secondary sulfate aerosol in the troposphere. Furthermore, the rate of sulfate formation had a turning point at about 250 K. The sulfate concentration at 250 K was about twice as large as that at 298 K. The rate of sulfate formation increased with decreasing temperature at temperatures above 250 K, while there is a contrary temperature effect at temperatures below 250 K. The activation energy for heterogeneous oxidations at temperatures from 245 K to 230 K was determined to be $14.63 \pm 0.20 \text{ kJ mol}^{-1}$. Mechanism of temperature dependence was proposed and the atmospheric implications were discussed.

1 Introduction

Mineral aerosol is an important component of airborne particulate matter (PM). Emitting into the atmosphere predominantly from arid and semiarid regions at a rate of 1000–3000 Tg per year (Harrison et al., 2001; Dentener et al., 1996), it has been by mass one of the largest sources to the global budget of PM (Rossi, 2003). Mineral aerosol may be transported over thousands of kilometers (Prospero, 1999) and therefore found far away from their sources resulting in a global distribution of this kind of

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atmospheric aerosols (Husar et al., 2001). Even at altitudes of 10 to 12 km, up to 500 part per trillion (ppt) of mineral ions (including Ca²⁺, Mg²⁺, Na⁺ and so on) can be found in the aerosol samples (Tabazadeh et al., 1998; Talbot et al., 1998; Cavaliere et al., 2010), indicating that these particles are also transported into the upper troposphere. During this process, mineral aerosol with atmospheric lifetimes of weeks (Prospero, 1999) plays a central role in global geochemical cycles as well as in climate change (Usher et al., 2003). It could affect the Earth's temperature either directly, by scattering and absorbing radiation (Li et al., 1996), or indirectly, by serving as cloud condensation nuclei (Cziczo et al., 2004; Koehler et al., 2010). In addition, mineral aerosol provides reactive sites for condensation and surface-mediated heterogeneous reactions with atmospheric trace gases and thus acts as sinks or sources for various atmospheric chemical species (Wagner et al., 2008). Recent atmospheric chemistry modeling studies (Dentener et al., 1996; Jacob, 2000; Zhang and Carmichael, 1999) have predicted that mineral aerosol can alter the chemical balance of the atmosphere through heterogeneous reactions.

Sulfur dioxide is one of important atmospheric trace gases that can react with mineral aerosol (Usher and Grassian, 2001; Zhang et al., 2006; Li and Han, 2010). As a well-known deleterious anthropogenic pollutant in the atmosphere, SO₂ is released to the troposphere by fossil fuel combustion, volcanic emissions, oxidation of DMS, and other sulfur compounds of biogenic origin (Seinfeld, 1998). The SO₂ concentration is about 50 to 100 ppt in the lower stratosphere, 50 ppt in the free troposphere, and as high as 160 ppt in North America clean continental air (Seinfeld, 1998). It is estimated that nearly half of global sulfur dioxide emissions are converted to particulate sulfate (Levin et al., 1996). It is critical to understand the formation of sulfate particles in the troposphere because of their health effects and their direct and indirect effects on radiative forcing, and hence on climate (Laskin et al., 2003).

There have been a number of models applied to predict the formation of sulfate aerosols on global scale (Langner and Rodhe, 1991; Pham et al., 1995; Kasibhatla et al., 1997), and the results revealed a systematic tendency of the model to overestimate

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SO₂ concentrations and underestimate sulfate concentrations (Kasibhatla et al., 1997). Two well-known routes for SO₂ oxidation to sulfate are via gaseous oxidation by OH radicals (Seinfeld, 1998) and aqueous oxidation in cloud or fog droplets (Rattigan et al., 2000; Botha et al., 1994). But these two mechanisms are not enough to bridge the gap between field and model studies (Luria and Sievering, 1991). Recently, field measurements have found that most of the global mineral aerosol surface was coated with sulfate (Zhang et al., 2000; Zhuang et al., 1999). There is a correlation between particulate sulfate and mineral aerosol (Zhuang et al., 1992; Nishikawa et al., 1991) and such a correlation could be caused by the surface reactions transferring SO₂ to SO₄²⁻ (Xiao et al., 1997; Song and Carmichael, 1999). Thus, the heterogeneous oxidations of SO₂ to sulfate on mineral aerosol have gotten more and more attention in recent years (Dentener et al., 1996; Kasibhatla et al., 1997; Usher et al., 2003). A number of different substrates such as Saharan dust (Ullerstam et al., 2002), China loess (Usher et al., 2002), and some metal oxides (Goodman et al., 2001; Usher et al., 2002; Al-Hosney and Grassian, 2005; Li et al., 2006; Fu et al., 2007; Baltrusaitis et al., 2007; Ge et al., 2009; Fu et al., 2009) were used to study the kinetics and mechanisms of heterogeneous SO₂ oxidation to sulfate. Particles properties (e.g., particles composition and size distributions), the reactive uptake coefficients, and mechanisms were considered in these studies. It is found that atmospheric conditions such as, temperature, relative humidity and light irradiation play an important role in sulfate formation. To our knowledge, however, most of previous work was performed at room temperature. There is no direct study of the heterogeneous oxidation of SO₂ on mineral dust at temperatures less than 298 K. Although room temperature studies are useful for understanding the mechanisms of the heterogeneous oxidation of SO₂ in the lower troposphere, information on the temperature dependence of this reaction rate are still needed for predicting the seasonal variation of sulfate.

In reality, the temperature in the Earth's atmosphere varies with latitude, longitude, and altitude above the Earth's surface, as well as the season and the time of day (Smith, 2003). The temperature at the troposphere can reach values much lower than

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220 K, down to 180 K above the Antarctic in winter (Smith, 2003; Toon et al., 1986). Laboratory studies of atmospherically important reactions over a wide range of temperatures, especially down to temperatures below room temperature, are desired. On the other hand, the measurement of reaction rate constants below room temperature can provide information that can be used directly in atmospheric models, without recourse to uncertain extrapolation over a limited temperature range using the Arrhenius expression, $k = A \exp(-E_a/RT)$. Thus the experimental determination of rate constants for important atmospheric reactions and how these rate constants vary with temperature remain a crucially important part of atmospheric science (Smith, 2003). Moreover, the seasonal variation of sulfate burden can have a significant effect on the direct radiative forcing of sulfate aerosols (Shaw and Paur, 1983; Feichter et al., 1996). Thus it is important to explore sulfate formation as a function of seasonal temperatures.

Calcium carbonate is an important and ubiquitous mineral in biological and geochemical systems (Al-Hosney and Grassian, 2004). In addition to influencing on global CO₂ exchange (Ridgwell and Zeebe, 2005), calcium carbonate is a reactive component of mineral aerosol in the troposphere (Usher et al., 2003) and heterogeneous reactions of trace gases with carbonates can alter the chemical balance of the atmosphere (Hanisch and Crowley, 2001; Goudie and Middleton, 2001; Al-Hosney and Grassian, 2004; Laskin et al., 2005). In coal-burning power plants, 75–98% of the SO₂ generated by combustion is removed by reaction with wet or dry limestone, which is predominantly composed of CaCO₃ (Srivastava and Jozewicz, 2001).

On the basis of above reasons, the influence of temperature on the heterogeneous oxidation of SO₂ by O₃ on CaCO₃ particle was investigated. Using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), the series reactive uptake coefficients for the heterogeneous oxidations of SO₂ by O₃ on the surface of CaCO₃ particle at different temperatures were obtained. The reactive uptake coefficients at different temperatures will supply the basic data for model studies. Moreover, the mechanism of the temperature dependence of rate constants was also discussed. The results are helpful for further understanding the seasonal variation of secondary sulfate aerosols

as well as the spatial distribution of activity for the heterogeneous oxidation of SO₂ on mineral dust particle in the troposphere.

2 Experimental

2.1 Chemicals

5 Commercially available CaCO₃ particles were purchased from Alfa Aesar (with a stated purity of 99.5%). The Brunauer-Emmett-Teller (BET) surface area of the particles was measured to be 1.35 m² g⁻¹ (Autosorb-1-MP automatic equipment (Quanta Chrome Instrument Co.)). SO₂ (99.9%, Beijing Huayuan Gas Chemical industry Co., Ltd.) was diluted and mixed with N₂ (> 99.999%, Beijing Tailong Electronics Co., Ltd) before
10 used. O₂ (> 99.998%, Orient Center Gas Science & Technology Co., Ltd.) was used to simulate the ambient air. Ultrapure water with resistivity of 18.2 MΩ·cm was purified by the Thermo Scientific Barnstead EasyPure II systems (Model UF).

Ozone was generated by irradiating a dry flow of pure O₂ with an ultraviolet lamp (Heraeus Ltd., ZSZ-8). The ozone concentration was determined by Ozone analyzer
15 (Model 49i, Thermo Electron Corporation, UV Photometric technology). Before each experiment, the O₃/O₂ mixture flowed through the lamp compartment for 1 h to ensure that the ozone concentration was stable.

2.2 Gas supply system

The gas supply system was composed of four inlet lines which were made of Teflon
20 tube. The first line supplied diluted SO₂ mixed with N₂, and the concentration is 4.9 × 10¹⁴ molecules cm⁻³; the second one provided a mixture of ozone and oxygen; The third line provided O₂ for simulating the ambient air; and the fourth line was used to provide additional nitrogen gas for dilution. All gases were mixed together before entering the reactor chamber, resulting in a total flow of 400 sccm synthesized air (21% O₂ and

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79% N₂). N₂ and O₂ were dehumidified by silica gel and molecular sieve before flowing into the system, and the relative humidity (RH) was less than 1%. The SO₂ was diluted by N₂ in a glass bottle and the partial pressures were monitored by absolute pressure transducer (MKS 627B range 0 to 1000 torr). Mass flow controllers (Beijing Sevenstar electronics Co., Ltd.) were used to adjust the flux of diluted SO₂ and N₂ to an expected concentration. The O₃ concentration in mixture was controlled by varying the flux of oxygen that exposed to UV light. The reactant flow was forced to pass through the CaCO₃ particles in the DRIFTS reactor. Average residence time of gases inside the DRIFTS cell was approximately 2.5 s.

2.3 Experimental methods

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used successfully for the analysis of solid, and it has now applied extensively to study the kinetics and mechanisms of the heterogeneous chemistry on particle surfaces (Vogt and Finlaysonpitts, 1994; Shaka et al., 2007; Li et al., 2006; Finlayson-Pitts, 2000). The advantage of DRIFTS is that it can be used to measure the reaction products in situ without interrupting the reaction processes (Finlayson-Pitts, 2000). DRIFTS can provide mechanistic details not available through other methods and the kinetics data can also be obtained (Vogt and Finlaysonpitts, 1994), and it was also possible to determine the reactive uptake coefficient by calibrating the infrared absorbance with ion chromatographic analysis of reacted samples. In this paper, DRIFTS was used to probe the SO₂ oxidation by O₃ on CaCO₃ particles at different temperatures.

A Nicolet FTIR Spectrometer 6700 equipped with a liquid-nitrogen-cooled narrow band mercury-cadmium-telluride (MCT) detector and the Praying Mantis accessory (Model DRP, Harrick Scientific Corp.) was applied to record in situ DRIFTS spectra in the spectral range from 4000 to 650 cm⁻¹. The low temperature reaction chamber (Model CHC-CHA-3, Harrick Scientific Corp.) was used in this study. This reaction chamber is designed for operation from -150 °C up to 600 °C under vacuum. The temperature of the sample cup could be measured by a thermocouple located directly

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underneath. The low temperature of the sample could be controlled by a balance of liquid-nitrogen cooling and resistive heating using an automatic temperature controller (ATC-024-2, Harrick Scientific Corp.). The sample cup is thermally isolated from the outer chamber wall. To prevent the ZnSe windows from frosting, a circulating water jacket was used to maintain the temperature of the outer surface of the chamber and windows at room temperature during low temperature operation.

To obtain reproducible packing of the DRIFTS sampling cup, the CaCO₃ powder (about 60 mg) was placed in the stainless steel cup (10 mm diameter, 0.5 mm depth) and compressed in order to form a solid pellet. SO₂ and O₃ with specific concentration in the dry synthetic air were then introduced as gaseous reactants. The experimental conditions were controlled at ambient pressure under dry synthetic air at temperatures from 230 to 298 K. In order to avoid a temperature difference between the sample holder and the solid sample, the system was thermostabilized for at least 1 h before each experiment. During the whole experiment process, the temperature uncertainty was ±1 K.

A typical experiment at each temperature lasted 200 min. The spectra were recorded at a resolution of 4 cm⁻¹, and 100 scans were usually averaged for each spectrum corresponding to a time resolution of 40 s. All the spectral data were automatically collected by Series program in OMINC software (Nicolet Corp.) in the experimental time. Simultaneously, the integrated absorbance of selected spectral features was obtained.

The products formed on CaCO₃ surface were analyzed by ion chromatography after reaction. The reacted particles were sonicated for 20 min in 1.5 mL of ultrapure water. The leaching water contained 1% formaldehyde as a preservative to enable the analysis of sulfite as well as sulfate. The filtered solution was analyzed using a Dionex ICS 900 system, which was equipped with a Dionex AS 14A analytical column and a conductivity detector (DS5).

3 Results and discussions

In order to explore the dependence of rate constant on the temperature for the oxidation of SO₂, the following aspects must be investigated. First, the products formed in the reaction at different temperatures must be identified. Second, how did the parameters of kinetics vary with the temperature.

3.1 Observed products

The sample was pretreated by heating in synthesized air at 573 K for 3 h before an experiment. This treatment gives stable conditions and also removes adsorbed species such as loosely bonded water, from the surface (Koretsky et al., 1997). After the pretreated sample was cooled to the desired experimental temperature, a background spectrum of the unreacted sample in the reaction chamber was collected. Spectra of surface products were then collected and shown as positive bands. When CaCO₃ particles were exposed simultaneously to SO₂ (4.9×10^{14} molecules cm⁻³) and O₃ (4.9×10^{14} molecules cm⁻³) for 200 min at different temperatures under dry conditions (RH < 1%), four new peaks were observed at 1198, 1127, 1090, and 995 cm⁻¹, as shown in Fig. 1. Assignments of the absorbance peaks were facilitated by examination of spectra in the literature that involved the reactions of SO₂ on mineral surface (Martin et al., 1987; Steger and Schmidt, 1964; Peak et al., 1999; Li et al., 2006). These new peaks were assigned to the stretching motion of adsorbed sulfate (SO₄²⁻) on the surface. With the FTIR technique, there are two infrared sulfate vibrations that are accessible to spectroscopic investigation in the mid-infrared region. They are the non-degenerate symmetric stretching ν_1 and the triply degenerate asymmetric stretching ν_3 bands (Peak et al., 1999). When the heterogeneous oxidation of SO₂ on the surface of CaCO₃ occurred, the ν_1 band was weakly active and appeared at 995 cm⁻¹. The ν_3 band split into three peaks, 1198, 1127, and 1090 cm⁻¹, respectively. The sulfate formed on CaCO₃ was also proved by the ion chromatography (IC).

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The infrared spectrum of the sulfate depends on its symmetry, while the symmetry of the adsorbed sulfate changes depending on whether it is monodentate or bidentate (Fu et al., 2007). In case of monodentate surface structure, sulfate adsorbs to a mineral surface through one oxygen atom, resulting in C_{3v} symmetry. Thus the ν₁ band becomes active at about 975 cm⁻¹, and ν₃ band splits into two peaks which are present above 1000 cm⁻¹ (Hug, 1997). If sulfate is bound to the surface through two oxygen atoms, forming a bidentate surface sulfato-metal complex, the symmetry of the sulfate is lowered to C_{2v} (Rubasinghege et al., 2010). For this symmetry, the ν₃ band splits into three peaks between 1050 and 1250 cm⁻¹, while the ν₁ band is shifted to about 1000 cm⁻¹ (Peak et al., 1999; Martin et al., 1987). According to the peak splitting information supplied by Fig. 1, the bidentate structure of sulfate on CaCO₃ was proposed at temperatures from 230 to 298 K.

To probe the details of the SO₂ surface oxidation by O₃ on the surface of CaCO₃, several sequential exposure experiments were designed in this study. The experiments in which three temperatures were chosen for modes included two steps, namely the sequential exposure to SO₂ and O₃. In the first experiment, SO₂ was introduced to the flow system alone with dry synthetic air (RH < 1%). The absorption bands present in the spectra shown in Fig. 2, curve a, b, and c can be assigned with the aid from previous infrared studies of SO₂ absorption on surfaces (Prince et al., 2007; Al-Hosney and Grassian, 2005; Li et al., 2006; Ullerstam et al., 2002; Martin et al., 1987; Usher et al., 2002). The broad band between 1000 and 885 cm⁻¹ in the CaCO₃ spectrum is composed of more than one peak and is corresponded to the absorptions of sulfite (SO₃²⁻) on the surface. Our experiment results showed that sulfite was the major product when CaCO₃ was exposed to SO₂ under dry air. In the absence of water, the presence of surface adsorbed sulfite was confirmed from observation of the characteristic IR absorption bands (Al-Hosney and Grassian, 2005). Then the SO₂ flow was cut off, and O₃ was introduced into the reaction system after the adsorption of SO₂ for 120 min. The broad band between 1000 and 885 cm⁻¹ disappeared in a few minutes while the one between 1240 and 1012 cm⁻¹ that assigned to sulfate appeared (Fig. 2d, e and f).

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The ion chromatography (IC) was used to confirm the formation of sulfite and sulfate. A sharp sulfite peak was found in IC chromatogram when SO₂ was absorbed alone, while there was only sulfate band after introducing O₃. This experiment indicated that SO₂ can adsorb on CaCO₃ surface to form sulfite and then sulfite can immediately be oxidized to sulfate in the presence of ozone. In the second experiment, the exposure sequence was changed. When O₃ was solely introduced over the particles surface, IR spectroscopy did not detect O₃ species adsorbed on surface after the adsorption of O₃ for 60 min. Then the O₃ flow was stopped and SO₂ was introduced to the reaction system. DRIFTS spectra showed the sulfate absorption bands were weak and the major products were sulfite. The ion chromatographic analysis of the leachate obtained immediately after the reaction showed the presence of sulfite and little sulfate appear. Therefore, O₃ just reversibly adsorbed on the surface of CaCO₃ in absence of SO₂, which was also demonstrated by other studies (Ullerstam et al., 2002; Li et al., 2006).

3.2 Temperature effects

The effects of temperatures (230 to 298 K) on the heterogeneous oxidation of sulfur dioxide (4.9×10^{14} molecules cm⁻³) by ozone (4.9×10^{14} molecules cm⁻³) on CaCO₃ at ambient pressure had been studied. The results showed that the transition state, the rate of sulfate formation, and the uptake coefficient were sensitive to the temperature.

3.2.1 Temperature effect on the transition state

The kinetics of the heterogeneous oxidation of SO₂ by O₃ on the surface of CaCO₃ particle were followed using the integrated absorbance-reaction time behavior instead of Kubelka-Munk function which is known to give to unacceptable uncertainty levels in quantitative experiments (Vogt and Finlaysonpitts, 1994; Samuels et al., 2006). The integrated absorbance of 1012–1240 cm⁻¹ for sulfate formed during the reaction at series temperatures as functions of reaction time are shown in Fig. 3. Two stages, the initial state and the steady state, were usually considered for the kinetics study

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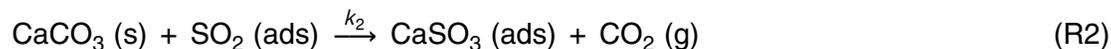


at room temperature (Li et al., 2006; Ge et al., 2009). As showed in Fig. 3, these two stages are observed at temperatures from 230 to 298 K. As soon as the reactive gas was introduced into the particle layers, the IR bands increased quickly, and the initial state emerged. After a certain time, when the IR bands increased at a stable speed the steady state was determined. However, an interesting stage which lasted about 80 min was observed at temperatures range from 230 to 257 K in present study. During this stage, the IR bands increased a little slower than initial state while faster than the steady state. This stage was named as transition state. As the temperature increase, the transition state lasted for shorter time. For temperatures above 257 K, the initial state transformed to the steady state so quickly (in minutes) that the transition state became gradually ambiguous. Hence, there may be physical-chemical processes which influence the reaction in a different way as a function of temperature.

According to the analysis and the results of our experiments, three major steps are proposed for the heterogeneous oxidation of SO₂ by O₃ on the surface of CaCO₃ particles. The first proposed step is the rapid adsorption of gas-phase SO₂ to the surface of CaCO₃. The reaction is expressed in Reaction (R1), where the (g) and (ads) symbols denote gas-phase and adsorbed-phase, respectively.

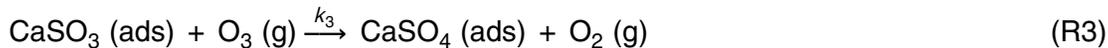


The second step is the direct reaction of adsorbed-phase SO₂ with the CaCO₃ surface to yield sulfite ion and CO₂. The reaction between SO₂ and CaCO₃ is thermodynamically favorable (Usher et al., 2002). On the surface of dry CaCO₃, SO₂ → SO₃²⁻ conversion takes place via the direct transfer of O²⁻ from CO₃²⁻ to a adsorbed-phase SO₂ molecule (Thompson and Palmer, 1988; Krebs and Nathanson, 2010). The reaction of adsorbed-phase SO₂ with the CaCO₃ can be expressed as



Finally, the sulfite rapidly oxidized to sulfate in the presence of ozone. This reaction is

an irreversible and very quick (Li et al., 2006). The reaction can be expressed as



The Reaction (R2) is the rate determining step in the whole mechanism. At the beginning of the whole reaction, the coverage of adsorbed-phase SO_2 was relative low compared to the large number of reactive sites on the surface. Thus adsorbed-phase SO_2 converted rapidly to form the sulfite on the surface and then the initial state emerged. The rapid conversion of adsorbed-phase SO_2 to sulfite continued until sterically and energetically suitable sites usable for sulfite formation have been diminished (Low et al., 1971). Continued uptake of SO_2 leads to some further sulfite formation. The transition state appeared at temperatures from 230 to 257 K during this process, which means more sites with less activity on surface at lower temperature (Liu et al., 2010). But there is less thermal energy available for the reaction to overcome the activation energy, which will be calculated in Sect. 3.2.2. And then it may need more time to complete the whole reaction at low temperature. Thus the transition state lasted for a longer time and became more obvious at low temperature. After a certain time, more and more reactive sites were taken up by product so that the numbers of reactive sites available for reaction became less. Therefore the rate of sulfate formation slowed, resulting in the steady state.

3.2.2 Temperature effect on the rate of sulfate formation

Based discussion above, the rate of sulfate formation was deduced according to the steady-state approximation, which had been described in detail elsewhere (Li et al., 2006).

$$r = \frac{d\{\text{SO}_4^{2-}\}}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{SO}_2] = k [\text{SO}_2] \quad (1)$$

Where k is the rate constant: $k = \frac{k_1 k_2}{k_{-1} + k_2}$.

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The SO₂ concentration was kept constant (using a continuous flow) in present study. Ordinarily one may expect the reaction rate to decrease with temperature because the rate constant for the reaction decrease with temperature. However, it was found that the total effect on the rate of sulfate formation is first slow increase and then decrease as temperature decrease in present study. In order to quantify the rate of sulfate formation $d\{\text{SO}_4^{2-}\}/dt$, the amount of sulfate ions formed during the reaction on the particulate sample was determined by the DRIFTS calibration curves made by mixing the weighted pure CaSO₄ uniformly in CaCO₃ to a certain concentration. The rate of sulfate formation was translated from absorption units s⁻¹ to SO₄²⁻ s⁻¹ by a conversion factor obtained from a calibration plot (Fig. 4). The plot shows that over a large concentration range the DRIFTS signal is proportional to sulfate concentration. And the plot gives a conversion factor that enables calculation of the amount of sulfate formed during the reaction. The sulfate ions concentrations:

$$(\text{integrated absorbance}) \times f = \{\text{SO}_4^{2-}\} \quad (2)$$

f was the conversion factor, and the calculated value for sulfate is 1.91×10^{18} ions g⁻¹ ABU⁻¹.

As can be seen in Fig. 5, the rate of sulfate formation increased with the decreasing of temperature in the range of 298 to 250 K, while it was reversed in the range of 250 to 230 K. That is, the rate of sulfate formation had a maximum value at about 250 K. To our knowledge, this kind of temperature effect on the heterogeneous oxidation of SO₂ is the first one reported. Previous literature (Koehler et al., 1999) did report that SO₂ adsorption on soot at colder temperatures leads to higher cover coverage compared to SO₂ adsorption on soot at room temperature. Several measurements have carried out to study SO₂ uptake onto ice and found it is enhanced at high temperatures (Clegg and Abbatt, 2001; Abbatt, 2003). However, it is scarce that turning point appears at the experimental temperatures. It indicates that it may involve more complicate processes at low temperature than at room temperature.

Figure 6 shows the linear regression of the rate of sulfate formation $d\{\text{SO}_4^{2-}\}/dt$ with the reciprocal value of temperature(1/ T). The correlation between the experimental

data and the generalized lines under least-square fitting is very good. The line has excellent correlation coefficient of > 0.999 . Therefore, the rate of sulfate formation $d\{\text{SO}_4^{2-}\}/dt$ at temperatures between 245 K and 230 K can be described in the form of the Arrhenius expression, $\ln d\{\text{SO}_4^{2-}\}/dt = 48.23 - 1759.24/T$. The activation energy for the reaction was determined to be $14.63 \pm 0.20 \text{ kJ mol}^{-1}$. Usually, the reactions with the activation energy greater than 20 kJ mol^{-1} are regarded to be too slow to play a significant role in atmospheric chemistry (Smith, 2003). It suggests that even the heterogeneous oxidation of sulfur dioxide by ozone on CaCO_3 at low temperature should not be neglected in the troposphere.

Two aspects are tried to interpret temperature effect on the rate of sulfate formation. On the one hand, there is less thermal energy available for the reaction than the one at high temperature (Koehler et al., 1999). It is more difficult to overcome the activation energy at lower temperature. According to the Arrhenius expression, the rate of sulfate formation will decrease as the temperature decrease. On the other hand, the reversible adsorption of gas-phase SO_2 is exothermic, and then the equilibrium (R1) would be pulled over to the right as the temperatures dropped (Clegg and Abbatt, 2001). It is implied that lower temperature leads to higher amount of adsorbed-phase SO_2 , which may make the heterogeneous reaction of SO_2 on CaCO_3 more easily. If only this factor is considered, the rate of sulfate formation would increase as the temperature decrease. A combination of these two aspects makes for the appearance of turning point. At temperatures from 298 to 250 K, the uptake enhancement of gas-phase SO_2 plays a leading role in the whole process and then the formation rate of sulfate increased with decreasing temperature. At temperatures below 250 K, a positive temperature effect on the reaction rate results from less thermal energy available for the reaction. Therefore, a maximum value of sulfate concentration on CaCO_3 was appeared at about 250 K.

After CaCO_3 particles were exposed simultaneously to SO_2 (4.9×10^{14} molecules cm^{-3}) and O_3 (4.9×10^{14} molecules cm^{-3}) for 200 min, the concentrations of sulfate ions at different temperatures was showed in Fig. 7. The concentrations of

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sulfate ions showed the similar trend as the rate of sulfate formation. It showed that the sulfate ions concentration varied with the temperature and reached a maximum value at a temperature near 250 K in the range of 230 to 298 K. The sulfate concentration at 250 K was about twice as large as that at 298 K. That is, the temperature affects the parameters of kinetics and then alters the concentration of secondary sulfate aerosol.

3.2.3 Temperature effect on uptake coefficient

To compare this study to others in the literature, the reactive uptake coefficient (γ) for the heterogeneous oxidation of SO_2 was deduced from the DRIFTS experiments. The reactive uptake coefficient, γ , is defined as the rate of product formation ($d\{\text{SO}_4^{2-}\}/dt$) divided by the rate of surface collisions per unit time (Z).

$$\gamma = \frac{d\{\text{SO}_4^{2-}\}/dt}{Z} \quad (3)$$

$$Z = \frac{1}{4} \bar{c} A_{\text{surface}} [\text{SO}_2] \quad (4)$$

$$\bar{c} = \sqrt{\frac{8RT}{\pi M_{\text{SO}_2}}} \quad (5)$$

Where \bar{c} is the mean molecular velocity of SO_2 , R is the gas constant, T is the temperature and M_{SO_2} is the molecular weight of SO_2 , A_{surface} is the effective sample surface. Concentrations marked with $\{ \}$ indicate surface species, whereas $[]$ indicate the concentration of gas-phase species.

It was suggested that two extreme cases of effective sample surface need to be considered for calculating the uptake coefficient (Li et al., 2006; Tong et al., 2010; Ullerstam et al., 2002). For the same heterogeneous reaction, the uptake coefficients can differ by about four orders of magnitude depending on the choice of the effective surface area (geometric or BET area) (Tong et al., 2010). If the reaction probability is high,

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the reactants would have no time to diffuse into the sample before reacting and the effective surface area will be the geometric surface area of the sample. If the reaction probability is low, the reactants may have enough time for diffusion into the entire sample and thus the BET surface area would more appropriately represent the effective area. When sulfate formed is evenly distributed into the sample, the uptake coefficients obtained using the geometric area will be overestimated. Therefore, the uptake coefficients obtained from the geometric and BET surface area as the reactive surface area should be respectively considered as upper and lower limits. Given BET surface area is in close approximation to the reactive surface under atmospheric conditions, the uptake coefficients are usually given and compared based on BET area (Borensen et al., 2000). However, the geometric surface area of the particles is usually used in the heterogeneous model studies because atmospheric models usually calculated aerosol surface area on the basis of the particle diameter. In order to compare with the results of other studies and to employ the atmospheric model, we have calculated two kinds of uptake coefficients based on BET and geometric areas respectively.

There have been several studies concerning the uptake of SO₂ and O₃ on different surfaces or materials using DRIFTS reactors (Ullerstam et al., 2002; Li et al., 2006, 2007; Ge et al., 2009), and most of them were deduced from results at room temperature. Uptake coefficients determined for SO₂ oxidation by O₃ on different particulates using a BET surface at room temperature are listed in Table 1. The data from Table 1 can be used for a comparison of the uptake coefficients for SO₂ in the presence of O₃ at room temperature with different experiment studies. For the different substances, the uptake coefficients can differ by about one order of magnitude using the same type of measurement technique. However, our experiment result $\gamma_0 = 1.27 \times 10^{-7}$ at room temperature was close to that with $\gamma_0 = 1.4 \times 10^{-7}$ on CaCO₃ particle (Li et al., 2006). It indicated that our experiments were valid. The little difference in uptake coefficient was likely caused by many factors such as, experimental artifacts, the way of measurement evaluation, and the difference between the BET surface area (the particles used by Li et al. (2006) was $1.95 \text{ m}^2 \text{ g}^{-1}$, while our particles was $1.35 \text{ m}^2 \text{ g}^{-1}$).

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The reactive uptake coefficients at temperatures from 230 to 298 K are listed in Table 2. Since the transition state was ambiguous at temperatures above 257 K, The transition state uptake coefficient (γ_{ts}) at temperatures from 263 to 298 K are not given. The reactive uptake coefficients at these different temperatures can be used directly in the model studies to predict the formation of secondary sulfate aerosol in the troposphere. As showed in Table 2, the reactive uptake coefficients are sensitive to the temperature. Both of the initial state uptake coefficient (γ_0) and the steady state uptake coefficient (γ_{ss}) are found to increase with the decrease of temperature at temperatures from 298 to 250 K, and decrease with the decrease of temperature at temperatures from 250 to 230 K. And the transition state uptake coefficient also has a maximum value at about 250 K. Thus, temperature should be paid more attention when studying the kinetics of the heterogeneous reaction.

Two factors, the mean molecular velocity of SO₂ and the rate constant of sulfate formation ($k = \frac{d\{SO_4^{2-}\}/dt}{[SO_2]}$ according to Eq. (1)), are related to temperature when the reactive uptake coefficients at different temperatures were calculated. On the basis of the Eqs. (2), (3), and (4), the reactive uptake coefficient would be proportion to $\sqrt{\frac{1}{T}}$ when $\frac{d\{SO_4^{2-}\}/dt}{[SO_2]}$ was kept constant. That is, if the mean molecular velocity of SO₂ is the only factor considered, the reactive uptake coefficients would monotonically increase with the temperature decrease and there would no maximum value appeared in the reactive uptake coefficients. Additionally, the reactive uptake coefficients had similar trend as the sulfate formation as a function of temperature, which have mentioned above. Therefore, the rate constant of sulfate formation instead of the mean molecular velocity of SO₂ may be a major factor that can be used to explain the effect of temperature on the reactive uptake coefficients.

4 Conclusions and atmospheric implications

In this study, the influence of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on CaCO_3 has been investigated by DRIFTS. Since the kinetics and mechanisms were determined at room temperature previously (Li et al., 2006), we focused attention on the question of whether the products depend on the temperature and how the rate of sulfate formation vary with the change of temperature in the range from 230 K to 298 K. The kinetics and mechanism of the heterogeneous oxidation were followed by monitoring IR spectral changes as a function of time. Compared to the reaction at room temperature, there is no new species observed on the surface at low temperature. However, we found that there existed an obvious transition state at temperatures from 230 to 257 K, while transition state was ambiguous at temperatures above 257 K. In addition, the rate of sulfate formation had a maximum value at about 250 K. The sulfate concentration at 250 K was about twice as large as that at room temperature. At temperatures above 250 K, the rate of sulfate formation increased with decreasing temperature. This is because of the uptake enhancement of gas-phase SO_2 at low temperatures. At temperatures below 250 K, less thermal energy available for the reaction resulted in a positive temperature effect on the reaction rate. The empirical formula between the rate of sulfate formation and temperature scope from 245 K to 230 K can be described in the form of the Arrhenius equation. That is, $\ln d\{\text{SO}_4^{2-}\}/dt = 48.23 - 1759.24/T$. The activation energy for the reaction was determined to $14.63 \pm 0.20 \text{ kJ mol}^{-1}$. The relatively low activation energy suggest the the heterogeneous oxidation of sulfur dioxide by ozone may still play an important role on the rate of sulfate formation even at low temperature.

As we noted in the introduction, the temperature in the Earth's atmosphere varies with latitude, longitude, and altitude above the Earth's surface, as well as the season and the time of day. The current research is only the first step toward understanding the sulfate formation in the real Earth's atmosphere. Additional studies are required in the laboratory studies. Nevertheless, the results in this study do point out that the rate

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of sulfate formation can be faster at low temperatures compared to room temperature. It is in accord with the fact that serious air pollution episodes have occurred during late fall and early winter months, when T was low (Freiberg, 1974). A three-dimensional global model investigation of seasonal variation in the atmospheric burden of anthropogenic sulfate aerosols has also showed that wintertime column sulfate is predicted to exceed summertime column sulfate by heterogeneous chemical production (Kasibhatla et al., 1997). Therefore, the heterogeneous oxidation of SO₂ to sulfate should not be neglected in the whole troposphere, including the high troposphere with low temperature. Furthermore, our results also suggested that the temperature could affect the reactive uptake coefficient so that the temperature factor should be considered when the reactive uptake coefficient used in the model studies.

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Table 1. Reactive uptake coefficients determined for SO₂ oxidation by O₃ on different particulates using a BET surface at room temperature.

Gas	Particulates	Reference	γ_0
SO ₂ + O ₃	Saharan dust	Ullerstam et al. (2002)	5×10^{-7}
SO ₂ + O ₃	NaCl	Li et al. (2007)	4.3×10^{-8}
SO ₂ + O ₃	Basic Al ₂ O ₃	Ge et al. (2009)	7×10^{-7}
SO ₂ + O ₃	Neutral Al ₂ O ₃	Ge et al. (2009)	3×10^{-7}
SO ₂ + O ₃	Acidic Al ₂ O ₃	Ge et al. (2009)	2×10^{-7}
SO ₂ + O ₃	CaCO ₃	Li et al. (2006)	1.4×10^{-7}
SO ₂ + O ₃	CaCO ₃	This work	1.27×10^{-7}

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Table 2. Reactive uptake coefficient for SO₂ (4.9×10^{14} molecules cm⁻³) and O₃ (4.9×10^{14} molecules cm⁻³) on CaCO₃ at series of tropospheric temperatures.

T/K	Y ₀		Y _{ts}		Y _{ss}	
	Geometric 10 ⁻⁴	BET 10 ⁻⁷	Geometric 10 ⁻⁵	BET 10 ⁻⁸	Geometric 10 ⁻⁶	BET 10 ⁻⁹
298	1.31 ± 0.13	1.27 ± 0.13	–	–	1.87 ± 0.14	1.81 ± 0.11
283	1.32 ± 0.10	1.28 ± 0.10	–	–	2.46 ± 0.32	2.37 ± 0.29
273	1.62 ± 0.10	1.56 ± 0.09	–	–	2.31 ± 0.31	2.23 ± 0.30
263	1.78 ± 0.05	1.73 ± 0.05	–	–	3.35 ± 0.17	3.24 ± 0.16
257	2.27 ± 0.20	2.19 ± 0.19	2.16 ± 0.47	2.09 ± 0.46	5.70 ± 1.06	5.53 ± 1.02
250	2.44 ± 0.07	2.36 ± 0.07	2.86 ± 0.24	2.78 ± 0.24	6.12 ± 1.12	5.93 ± 1.08
245	2.45 ± 0.28	2.37 ± 0.28	2.38 ± 0.13	2.30 ± 0.16	5.53 ± 0.99	5.35 ± 0.97
240	2.15 ± 0.28	2.08 ± 0.28	1.75 ± 0.32	1.69 ± 0.31	3.81 ± 0.54	3.69 ± 0.532
230	1.59 ± 0.13	1.53 ± 0.13	0.60 ± 0.20	0.58 ± 0.19	4.11 ± 1.06	3.98 ± 1.02

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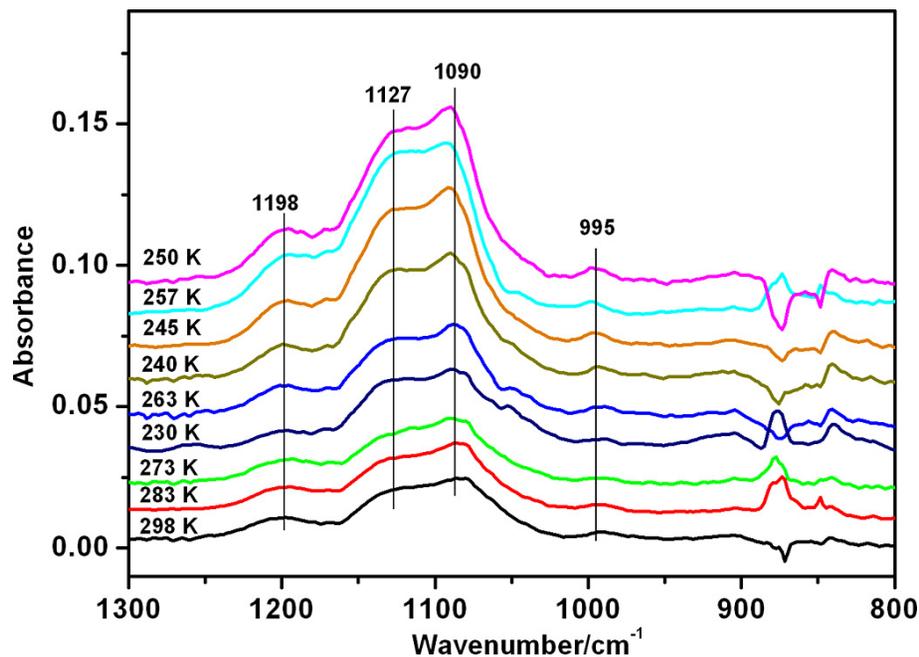


Fig. 1. In situ DRIFTS spectra (absorbance units) recorded after 200 min of the reaction of SO₂ and O₃ on CaCO₃ at different temperatures under dry conditions (RH < 1%).

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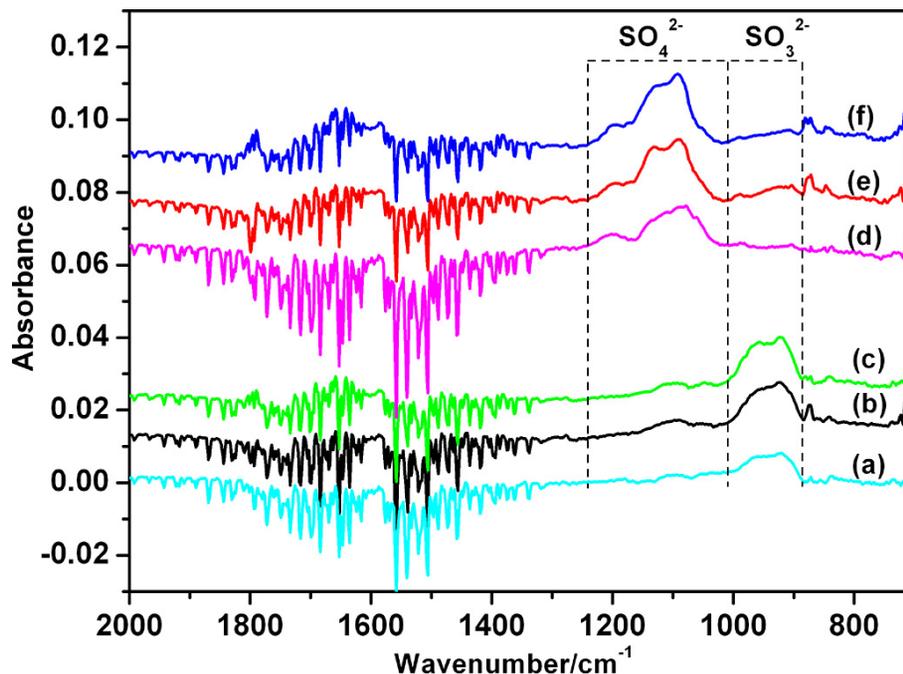


Fig. 2. The in situ DRIFTS spectra recorded during the sequential exposure experiment to SO₂ and O₃. (a), (b), (c) showed the product spectra when the adsorption rate becomes stable after addition of SO₂ at 298 K, 263 K and 250 K, respectively. (d), (e), (f) show the product spectra when the SO₂ flow was cut off, and O₃ was introduced into the reaction system for 60 min at 298 K, 263 K and 250 K, respectively.

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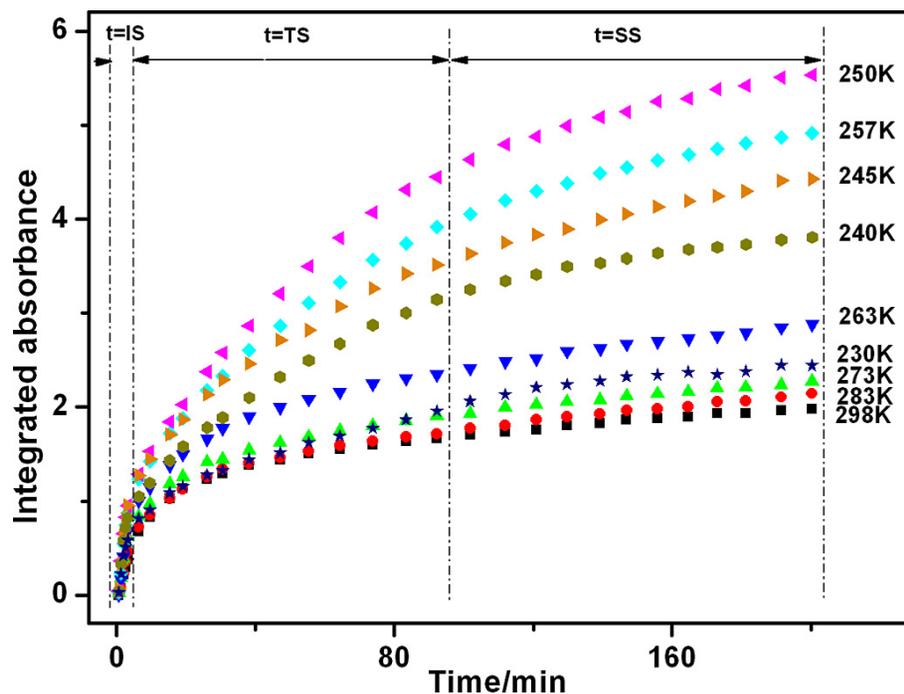


Fig. 3. The integrated absorbance of 1012–1240 cm⁻¹ for sulfate formed during the reaction at series temperatures as functions of reaction time. IS, TS, SS stand for the initial state, the transition state, and the steady state, respectively.

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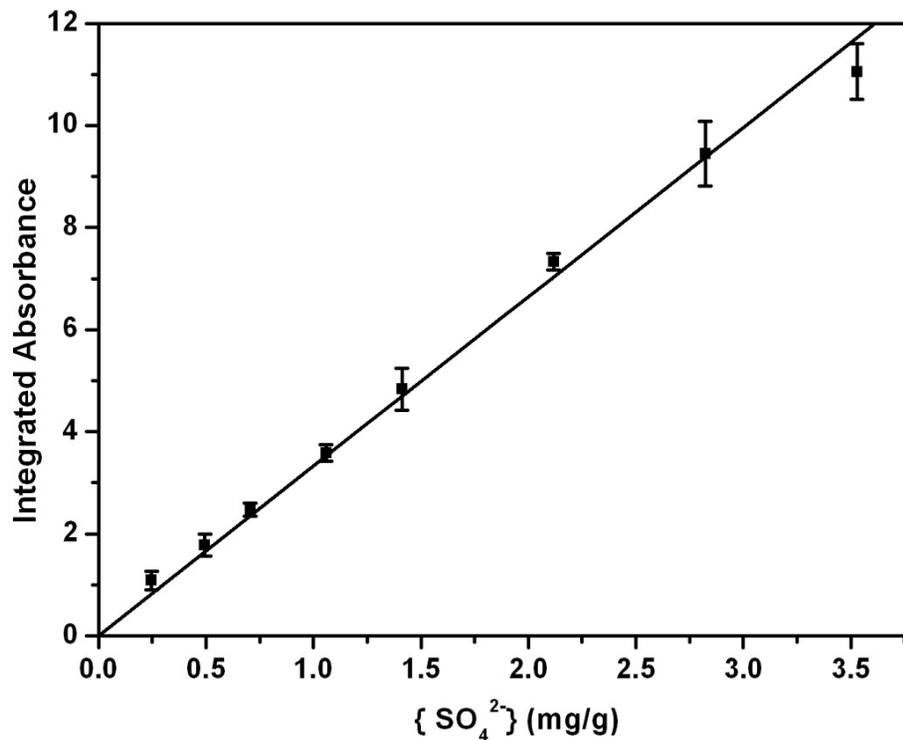


Fig. 4. Calibration curve for the integrated absorbance versus the concentration of sulfate.

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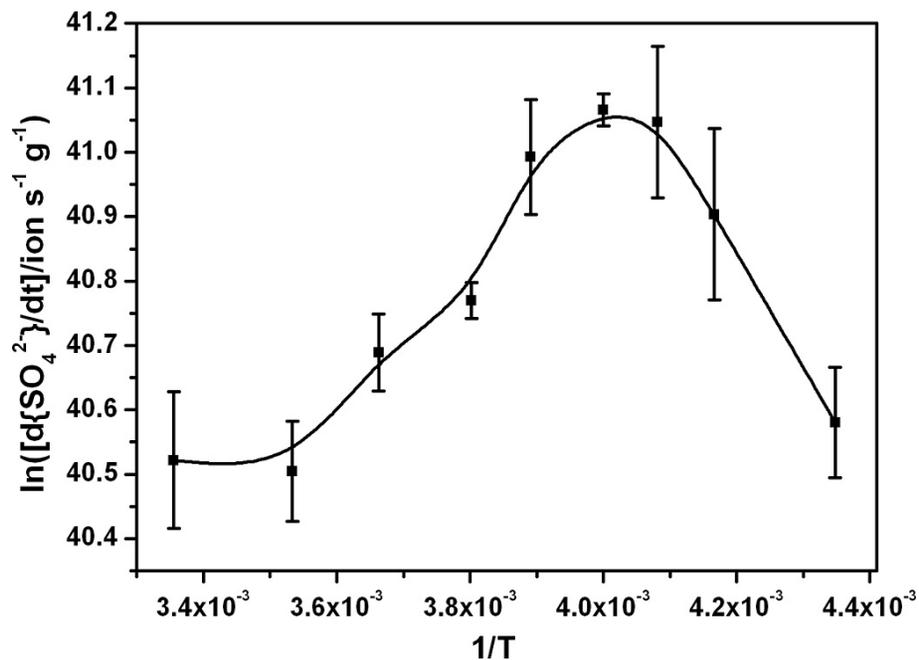


Fig. 5. The relationship between formation rate of sulfate and temperature.

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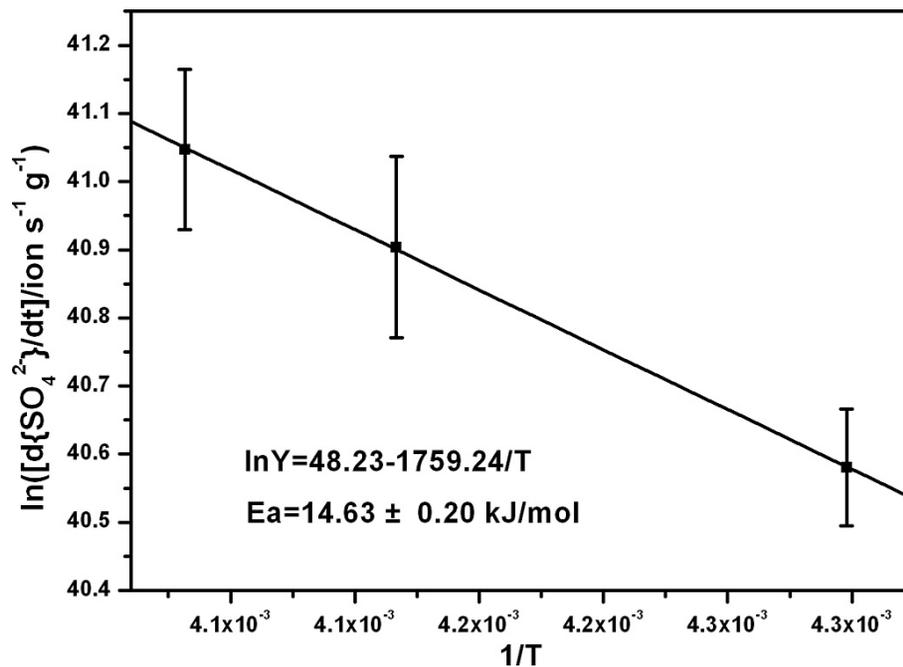


Fig. 6. The linear regression of the rate of sulfate formation $d\{\text{SO}_4^{2-}\}/dt$ with the reciprocal value of temperature ($1/T$).

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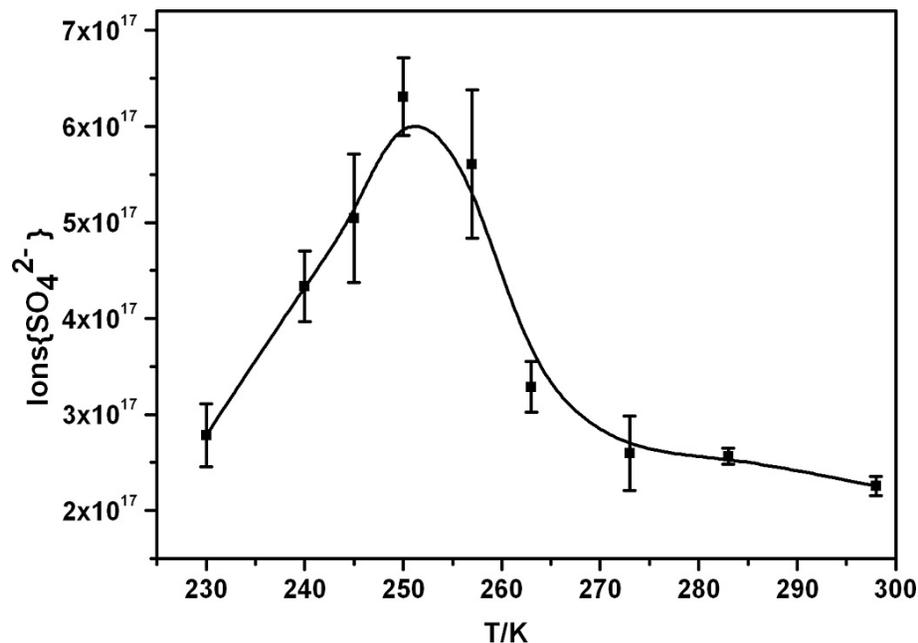


Fig. 7. The concentrations of sulfate ions at different temperatures after CaCO₃ particles exposed simultaneously to SO₂ (4.9×10^{14} molecules cm⁻³) and O₃ (4.9×10^{14} molecules cm⁻³) for 200 min.

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