Mechanism of Heterogeneous Oxidation of Carbonyl Sulfide on Al₂O₃: An in Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy Investigation

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Heterogeneous reaction of carbonyl sulfide (OCS) on the surface of different types of alumina (Al₂O₃) at 298 K was investigated in a closed system and a flowed system using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The effects of calcination temperature of the Al₂O₃ on its catalyzed reactivity were studied. The crystal structure and surface area of the Al₂O₃ were characterized using X-ray diffraction (XRD) and the Brunauer—Emmett—Teller (BET) method. This paper revealed that adsorbed OCS could be catalytically oxidized on the surface of Al₂O₃ to form gas-phase CO₂ and surface hydrogen carbonate (HCO₃⁻) and sulfate (SO₄²⁻) species at 298 K. The surface hydroxyl (OH) species on the Al₂O₃ had been found to be the key reactant for the heterogeneous oxidation of OCS. Furthermore, the surface hydrogen thiocarbonate (HSCO₂⁻) species, an intermediate formed in the reaction of OCS with OH, can be observed on the thermal-treated Al₂O₃. On the basis of these results, the reaction mechanism of heterogeneous oxidation of OCS on Al₂O₃ is discussed.

1. Introduction

Carbonyl sulfide (OCS) is the most abundant atmospheric sulfur containing gas in the remote troposphere.¹,² It is relatively inert in the troposphere, and it can be transported into the stratosphere where its photooxidation is considered to be an important source of stratospheric sulfate during volcanically quiescent periods.³⁻⁵ From the point of view of the environment, it is important to study the global OCS cycle. Most studies focus on the homogeneous reaction of OCS with OH in the gas-phase and the consumption of OCS by the plants, soil, etc.⁶ Heterogeneous interactions between gaseous molecules with wet or dry aerosol particles have gained considerable interest since they have the potential to alter the process of atmospheric chemistry significantly.⁶,⁷ The surface of oxide particles in the atmosphere can adsorb and catalyze reactions of trace gases and, thus, change the chemical balance of the atmosphere.⁷,⁸

Aluminum is one of the most abundant elements in atmospheric particles. It has been reported that alumina (Al₂O₃) surface catalyzes the oxidation of H₂S or CS₂.⁹,¹⁰ However, to our knowledge, very few studies have examined the possibility of heterogeneous reaction and the conversion pathway of OCS on the surface of atmospheric particles. Therefore, we studied the reaction mechanism of OCS on the surface of Al₂O₃ as a simplified model. To understand the mechanism of heterogeneous reaction of OCS on the Al₂O₃ surface, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used in this study. DRIFTS can be used to observe the nature of the interaction of gas with a solid surface. In addition, in situ DRIFTS is especially useful to explore mechanisms of heterogeneous reactions of gases on a solid surface by providing information on reactive intermediates formed on the surface.

The present paper is devoted to a systematic in situ DRIFTS study on the mechanism of the heterogeneous reaction of OCS on the surfaces of four types of Al₂O₃. The surface hydrogen carbonate (HCO₃⁻), hydrogen thiocarbonate (HSCO₂⁻), and sulfate (SO₄²⁻) species were found to be the major products formed from heterogeneous oxidation of OCS on the surface of Al₂O₃. On the basis of the experimental results, a composite reaction mechanism of heterogeneous oxidation of OCS on Al₂O₃ is proposed.

2. Experimental Section

2.1. Materials. Four types of Al₂O₃ used in this experiment were prepared from boehmite (AlOOH, Shandong aluminum Corporation) by calcining at different temperatures. The samples of Al₂O₃-A, Al₂O₃-B, Al₂O₃-C, and Al₂O₃-D were obtained by calcining AlOOH at 573, 873, 1273, and 1473 K for 3 h, respectively. Before DRIFTS measurement, all Al₂O₃ samples were pretreated in an in situ infrared cell by heating in 100 mL/min of O₂ at 873 K (except the Al₂O₃-A sample which was heated at 573 K) for 3 h.

All reactant gases were used without further purification as follows: Carbonyl sulfide (OCS, 2%, OCS/N₂, Scott Specialty Gases Inc.), O₂ (99.99% purity, Beijing AP BEIFEN Gases Inc.).

2.2. Techniques of Characterization. BET Experiment. The nitrogen adsorption—desorption isotherms were obtained at 77 K over the whole range of relative pressures, using a Micromeritics ASAP 2000 automatic equipment. Specific areas were computed from these isotherms by applying the Brunauer—Emmett—Teller (BET) method.

X-ray Diffraction Experiment. The samples were characterized by X-ray diffractometry using a computerized Rigaku D/max-RB diffractometer (Japan, Cu Ka radiation, 1.54056 nm). The step scans were taken over a 2θ range of 10°–90° in steps of 0.02°/s.

In Situ DRIFTS Experiment. In Situ DRIFTS spectra were recorded on a NEXUS 670 (Thermo Nicolet Instrument Corporation) FT-IR, equipped with an in situ diffuse reflection spectrometry attachment.
chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N₂. The sample (about 11 mg) for the in situ DRIFTS studies was finely ground and placed into a ceramic crucible in the in situ chamber. The total flow rate was 100 mL/min in all the flow systems, and the volume of the closed system was 30 mL. The reference spectrum was measured after the pretreated sample was cooled to 298 K in a purified O₂ stream. The infrared spectra were collected and analyzed using a data acquisition computer with OMNIC 6.0 software (Nicolet Corp.) installed. All spectra reported here were recorded at a resolution of 4 cm⁻¹ for 100 scans.

2.3. Calibration Curve of the Gas-Phase OCS Concentration. A series of in situ DRIFTS spectra at a steady state of the flow system with various concentrations of OCS (40–2000 ppm) were recorded at 298 K. The integrated areas of the absorption peak of gaseous OCS in the range of 1980–2000 cm⁻¹ have a linear correlation with the concentration of OCS gas ($R^2 > 0.99$). The concentration of gas-phase OCS was determined by measuring the in situ DRIFTS spectra peak areas of gaseous OCS.

3. Results and Discussion

3.1. Characterizations. BET. BET results are shown in Table 1. The surface areas of the AlOOH, Al₂O₃-A, Al₂O₃-B, Al₂O₃-C, and Al₂O₃-D samples were decreasing with the increasing calcination temperature.

X-ray Diffraction. The XRD patterns of all samples of Al₂O₃ and AlOOH calcined at 573, 873, 1273, and 1473 K are presented in Figure 1. The Al₂O₃-A sample shows a characteristic of an amorphous structure and still exists mainly as AlOOH. Signals due to the crystal structure of Al₂O₃ changes from $\gamma$- to $\theta$-Al₂O₃ at 2337 and 2361 cm⁻¹ [1]. The Al₂O₃-C sample exists mainly as the crystal of $\theta$-Al₂O₃, and the crystal of $\gamma$-Al₂O₃ is also observed in Al₂O₃-C. [12-13] The Al₂O₃-D sample exists mainly as the crystal of $\alpha$-Al₂O₃ evidence in line at 2θ = 43°, 35°, and 57°. [12-13] With rising of the calcination temperature, the crystal structure of Al₂O₃ changes from $\gamma$-Al₂O₃ to $\theta$-Al₂O₃ and then to $\alpha$-Al₂O₃. [14]

3.2. Heterogeneous Reaction of OCS on the Al₂O₃ samples in a Closed System. The Al₂O₃-A sample (AlOOH calcined at 573 K for 3 h) was exposed to a flow of 1000 ppm OCS + 95% O₂ at 298 K for 5 min, and then, the inlet and outlet were closed. The in situ DRIFTS spectra on the Al₂O₃-A sample were recorded as a function of time and are shown in Figure 2. Strong peaks of gas-phase OCS appeared at 2071 and 2052 cm⁻¹. [15,16] A pair of peaks of gaseous carbon dioxide (CO₂) was observed at 2337 and 2361 cm⁻¹. [17,18] The bands at 1647 and 1412 cm⁻¹ are due to ν₁(OCO) and ν₂(OCO) of surface HCO₃⁻ species, respectively, [15,17-19] and the very weak band at 1354 cm⁻¹ is assigned to surface SO₄²⁻ species. [20-24] It is also found that the peaks for gas-phase CO₂ and surface SO₄²⁻ species increased in intensity with time, while the peaks of gaseous OCS diminished. The bands for HCO₃⁻ were not grown apparently from 2 to 20 min, because the surface HCO₃⁻ species is the intermediate of OCS oxidation, and exist in a dynamic balance process of formation and consumption. These results suggest that OCS in O₂ can be finally converted into gas-phase CO₂ and surface SO₄²⁻ species on the Al₂O₃-A sample surface at 298 K.

The same set experiments were also carried out using the Al₂O₃-B ($\gamma$-Al₂O₃), Al₂O₃-C ($\theta$-Al₂O₃), and Al₂O₃-D ($\alpha$-Al₂O₃) samples, respectively. The gas-phase OCS concentrations shown
in Figure 3 were determined by comparing the OCS absorbance peak area with the calibration curve of the gas-phase OCS concentration. To distinguish the effect of the surface of the system on the loss of OCS, a control experiment was performed under the same conditions by replacing Al₂O₃ sample with a gold mirror. In this case, only a very weak change of the gas-phase OCS concentration was observed during the experiment, indicating that the system may consume a small quantity of OCS through the adsorption or the heterogeneous reaction catalyzed by the surface of the system. The concentration of gaseous OCS drastically decreases with the Al₂O₃-A sample, whereas it decreases mildly with the Al₂O₃-B, Al₂O₃-C, and Al₂O₃-D samples. It is thought that the surface area has an important influence on the absorption and reaction of OCS; however, the Al₂O₃-A and Al₂O₃-B samples have similar surface areas, but they exhibit different reaction rates. Therefore, there must be other factor affecting the decrease of OCS.

3.3. Dynamic State in Situ DRIFTS Study of OCS + 95% O₂ on the Al₂O₃-A Samples in a Flow System. To gain further information about the reaction of OCS on the Al₂O₃-A sample, in situ DRIFTS spectra of the Al₂O₃-A sample as a function of time were measured in a flow of 1000 ppm OCS + 95% O₂ at 298 K (Figure 4). Similar to Figure 2, the peaks due to surface HCO₃⁻ (1639 and 1412 cm⁻¹) and SO₄²⁻ (1333 cm⁻¹) were observed, and the intensities of these peaks increased with time during 120 min (Figure 4B). On the basis of the previous studies, the peak located at 1242 cm⁻¹ could be assigned as the vibration of surface HCO₃⁻ species or be assigned to surface HSO₃⁻ species. To confirm our assignments about the surface HCO₃⁻ and HSO₃⁻ species, the Al₂O₃-A sample was exposed to a flow of 1000 ppm CO₂ + 95% O₂ at 298 K. As can be seen in Figure 5B, the vibration peaks of surface HCO₃⁻ species were located at 1655 and 1404 cm⁻¹ on the Al₂O₃-A sample. While the Al₂O₃-A sample was exposed to a flow of
200 ppm SO₂ + 95% O₂ at 298 K, as shown in Figure 6B, the vibration peaks of surface HSO₃⁻ species were located at 1242 cm⁻¹. Therefore, we finally assigned the peak located at 1242 cm⁻¹ (in Figure 4B) to the vibration mode of surface HSO₃⁻ species instead of surface HCO₃⁻ species. The broad band centered at 3543 cm⁻¹ was assigned to the î(OH) stretching of adsorbed H₂O. The peak at 1639 cm⁻¹ was assigned to a combination band produced from î(C=O) of surface HCO₃⁻ species and î(OH) of adsorbed H₂O, and the peak at 1412 cm⁻¹ was assigned to î(C=O) of surface HCO₃⁻ species.

Meanwhile, it should be noted that introduction of 1000 ppm OCS led to a drastic increase in the intensity of negative peaks at 3740 and 3666 cm⁻¹ in Figure 4A. In the model proposed by Peri, these bands were attributed to the vibrations of surface hydroxyl (OH) species. The consumption of surface OH species meant that the reaction between OCS and surface OH must occur. However, other intermediates, favorable for understanding the mechanism of OCS conversion, were not measured in this rapid reaction. Considering that the thermal pretreatment of Al₂O₃ was expected to reduce the surface OH groups, further experiments were performed on the thermal pretreatment of Al₂O₃ samples to observe these intermediates.

Figure 7 shows the in situ DRIFTS spectra of the Al₂O₃-B sample in a flow of 1000 ppm OCS + 95% O₂ at 298 K. The bands at 1653 and 1423 cm⁻¹ due to the physically adsorbed OCS were observed at the beginning of the reaction and then diminished.
between the chemically adsorbed surface species (e.g. HCO$^-$) and the physically adsorbed OCS.

It is apparent that the thermal treatment of Al$_2$O$_3$ could slow OCS oxidation and enable the observation of the reaction intermediate. In the region of OH groups, a drastic increase in the intensity of negative peaks at 3772, 3732, and 3682 cm$^{-1}$ attributed to the vibrations of surface OH groups (Figure 7A) was observed. These results strongly suggest that the formation of surface HSCO$_2^-$ species is derived from the reaction between surface OH species and OCS. Although the thermal treatment of Al$_2$O$_3$ could reduce the surface OH species and the formation of surface HSCO$_2^-$ species, the conversion rate of surface HSCO$_2^-$ species into surface HSO$_3^-$ species under this condition might be decreased more greatly; thus, surface HSCO$_2^-$ species were clearly detected. This indicates that the surface OH species play an important role in the formation of surface HSCO$_2^-$ species and that the surface HSCO$_2^-$ species converted into surface HSO$_3^-$ and HCO$_3^-$ species also need the participation of the surface OH species.

To confirm the presence of surface HSCO$_2^-$ species as an intermediate of OCS oxidation, the same experiment was performed on the Al$_2$O$_3$-C sample (AlOOH calcined at 1273 K for 3 h). As shown in Figure 8, exposure of the sample to OCS resulted in the appearance of surface HCO$_3^-$ (1653 and 1435 cm$^{-1}$), HSCO$_2^-$ (1579 cm$^{-1}$), and SO$_4^{2-}$ species (1333 cm$^{-1}$) (Figure 8B), which was also accompanied by the formation of negative peaks at 3755 and 3678 cm$^{-1}$ due to surface OH groups (Figure 8A). Obviously, the oxidation of OCS shows the same mechanism on the Al$_2$O$_3$-B and Al$_2$O$_3$-C samples. However, high-temperature calcination of AlOOH resulted in an activity loss of catalytic oxidation for OCS, as evidenced by the lower reaction rate (Figure 3).

To further investigate the role of surface OH groups in OCS oxidation on Al$_2$O$_3$, the same experiment was performed on the
The heterogeneous oxidation of OCS through reducing the surface OH species, which is implied as the key reactant of the reaction.

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References and Notes