

The Effect of Metal Oxides Emitted by Motor Vehicles on the Formation of Secondary Components in Atmospheric Fine Particles

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Abstract: Based on the microscopic reaction of gaseous pollutants from motor vehicles on the surface of Metal particles, the adsorption states of NO_x and SO₂ on the surface of metal oxides under different conditions were simulated by diffuse reflectance infrared spectroscopy. The results show that NO_x, SO₂, and mixed NO_x / SO₂ gas react with oxygen vacancies and coordinated oxygen of Fe³⁺, respectively, and finally adsorb on the Fe₂O₃ surface in different forms of nitrate and sulfate. The surface pre adsorption water, the adsorption of nitrate and the catalytic reduction of Fe₂O₃ will affect the heterogeneous oxidation of SO₂. It is revealed that the emissions of motor vehicles contribute to the formation of fine particles in the atmosphere, which needs to be controlled at the source.

1. Introduction

The quality of the atmospheric environment is increasingly affecting the quality of people's lives, so that pollutants in the atmosphere have attracted the attention of many researchers. Among the air pollutants, fine particulate matter (PM_{2.5}) is most characteristic[1]. Various studies[2-7] have shown that the main components of vehicle exhausts are hydrocarbons (HC), nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO₂), lead compounds, benzopyrene, and solid particles, which are important sources of PM_{2.5} in the atmosphere. Among them, SO₂ and NO_x emissions dominate. In addition, there are metal elements, such as Al, Fe, Ni, Mn, and Ti, with high activity and a certain catalytic or photocatalysis ability for lubricating oil and fuel oil for motor vehicles. The metal oxide particles formed by oxidation of these metal elements can promote the adsorption of NO_x, SO₂, and HC in vehicle exhausts on the surface of these particles, forming nitrate, sulfate, organic acid salts, and other substances, which has a significant impact on the formation of fine particle pollution in the regional atmosphere.

However, there have been few studies on the effect of metal oxides emitted by motor vehicles on the formation of atmospheric fine particles. In addition, vehicles have entered many fields of

production and the people's life in China, resulting in a more significant impact on the atmospheric environment. Therefore, it is an urgent matter to study the formation of atmospheric fine particles via metal oxides emitted from motor vehicles. In addition, a study[8] showed that the substances in the motor vehicle engine are mainly composed of C and a variety of metal elements. Among them, the relative content of C is 90% - 98%, and Fe is the most abundant metal element, with a relative content of 1.01% - 3.07%. In view of the above analysis, in order to study the formation mechanism of PM2.5 secondary components by metal oxides emitted by motor vehicles under different dry and wet conditions, Fe, which contains more metal in carbon particles, is selected, and Fe is different from other oxidized particles. It has both photochemical activity and strong oxidation property, and can also realize NO_x and SO₂ oxidation by Fe cycle. The adsorption state of NO_x and SO₂ on Fe₂O₃ surface was analyzed by the oxidation state of Fe²⁺. This paper takes Fe as the target element, NO and SO₂ as the target gases, analyzes the influence of metal oxide particles (Fe₂O₃) on the formation of PM2.5 through laboratory simulation, reveals the formation mechanism of metal oxides, and thereby makes contributions to the prevention and control of vehicle air pollution.

2. Experimental Method

2.1. Sample Material

The purity of O₂ was 99.9997%, i.e., it was analytically pure, the N₂ gas had a purity of 99.99%, SO₂ had a purity of 99.99%, and NO had a purity of 99.99%. All gases were purchased from Fulian Technology Gas (Kunshan) Co., Ltd. The Fe₂O₃ powder was of analytical grade (AR) and purchased at Sinopharm Chemical Reagent Co., Ltd.

2.2. Experimental Device

Since diffuse reflectance infrared spectroscopy (DRIFTS) can detect the surface changes of particles very sensitively, this method has been widely used in the fields of catalytic oxidation and photochemistry[9-10]. Therefore, we used a Fourier transform infrared spectrometer (EQUINOX-55, German BRUKER company). The analysis was carried out on a Nexus 670 diffuse reflectance infrared analysis device produced by Nicholas. The schematic diagram of the experimental device is shown in Figure 1.

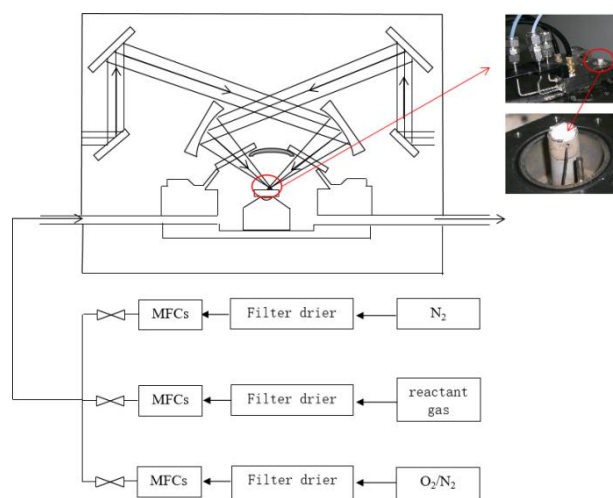


Figure 1: Diffuse reflectance infrared reaction test.

As shown in Figure 1, the diffuse reflectance infrared instrument is connected with an external gas distribution system, including three gas channels: N₂, reaction gas (NO / N₂, SO₂ / N₂, NO / SO₂ / N₂), and O₂ / N₂. After passing through the drying filter, the first three gases are regulated by mass flow controllers (MFCs), according to the test requirements before entering the diffuse reflectance infrared instrument. The main functions of each gas in the gas distribution system are as follows: N₂ is used to purge the instrument channel before the test to keep the pipeline clean; in addition, it is also used as a dilution gas; the reaction gas is the gas participating in the reaction; O₂ / N₂ is the mixed gas with various oxygen contents after being diluted by N₂.

2.3. Experimental Parameters

As shown in the Fig.1, The spectral range covered was 650-4000 cm⁻¹, the resolution was 4 cm⁻¹, and the number of scans was 256. The composition and flow of the reaction gas were controlled by a mass flow meter, with a total flow of 80 ml/min. In most experiments, the dilution gas is air, and pure oxygen and nitrogen are mixed to synthesize air. Before the start of the reaction, a certain amount of samples are evenly placed in the sample cup and placed in the diffuse reflectance infrared spectrum cell. The three gases in the experiment enter the reaction chamber through the dryer, and the gas is introduced into the laboratory. The interference beam incident on the sample and the light reflected from the sample is collected to record the infrared spectrum in the reaction process.

During the experiment, O₂ and N₂ were introduced into the reaction chamber by gas dryer. The selected gas concentration is the concentration of gaseous pollutants emitted from diesel engine exhaust gas - NO (1000 ppm, NO₂ / N₂), SO₂ (500 ppm, SO₂ / N₂) and O₂ (5% - 10%) are used as reaction gases [11]. The powder samples of Fe₂O₃ metal oxide used as reaction are pretreated, and the other part is not pretreated. The former is to place metal oxide in 350 °C for 1h in N₂. The latter is to put the particles directly into the diffuse reflection tank for treatment. The relative humidity of the samples is roughly the same as that in the atmosphere, so that the micro reaction differences between the metal oxide samples and the reaction gases can be compared under different dry and wet conditions, so as to conduct unified analysis. The whole design is to simulate the heterogeneous reaction between trace pollution gas and typical metal particles in the process of vehicle exhaust emission.

3. Results and Discussion

3.1. Adsorption State of NO_x on the Fe₂O₃ Surface

In this experiment, two operating conditions, aerobic and anaerobic, were selected to study the adsorption state of NO_x on the Fe₂O₃ surface, namely, the two systems of NO (1000 ppm) and NO (1000 ppm)/O₂ (10%). The analysis results are presented below.

3.1.1. Change of NO (1000 ppm) / N₂ on the Fe₂O₃ Surface

The dried Fe₂O₃ sample was placed in the diffuse reflection reaction tank, and was then passed into NO (1000 ppm) / N₂ for adsorption. The flow rate was 80 ml / min, the spectrum was emitted after 5 min of adsorption, and the emission time was 20 min. The results are shown in Figure 2.

As shown in Figure 2, the infrared spectrum up to 20 minutes of NO adsorption showed obvious absorption peaks at 1195cm⁻¹, 1286cm⁻¹, and 1619cm⁻¹, which increased with an increase in reaction time. Among the three obvious absorption peaks, that at 1195cm⁻¹ was strongest, followed by that at 1619 cm⁻¹, while that at 1286cm⁻¹ was weakest. From the point of view of the

coordination mode, the absorption peak at 1195 cm^{-1} can be attributed to monodentate nitrite [Fe-O-N-O], which is the V3 vibration of nitrite and adsorbed on the oxygen ion coordinated with Fe by the nitrogen atom during NO formation, indicating that this species may be the main product of adsorption[12]. However, weaker absorption peaks appeared at 1286 cm^{-1} and 1619 cm^{-1} , which can be attributed to bidentate nitrate [Fe-O₂NO] and bridge nitrate [(Fe-O)₂=NO][13], respectively. Therefore, NO can produce a variety of adsorbed substances on the surface of iron oxide, some of which are formed by the oxidation of NO by lattice oxygen in Fe₂O₃. These substances are adsorbed on the surface of iron oxide in various forms, which plays an important role in the further reaction with Fe₂O₃[14].

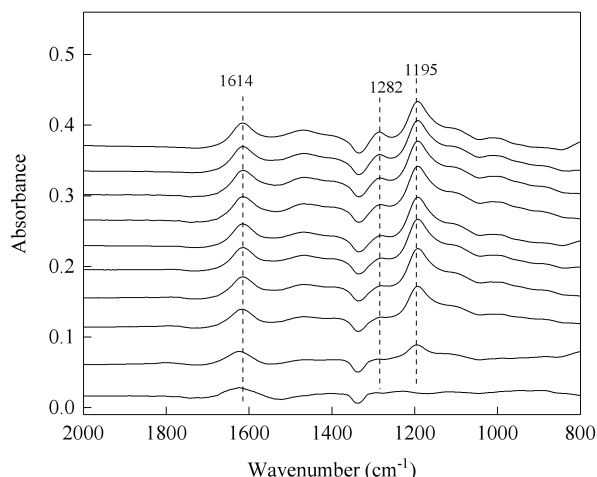


Figure 2: DRIFTS spectra of surface products as a function of reaction time during the reaction of Fe₂O₃ particle surfaces with NO(1000 ppm).

3.1.2. Change of NO (1000 ppm)/N₂ on the Fe₂O₃ Surface

The dried Fe₂O₃ samples were placed in a diffuse reflectance reaction cell and then supplied with NO (1000 ppm) / O₂ (10%) / N₂ for adsorption at a flow rate of 80 ml / min. with either dry or wet Fe₂O₃ samples. The samples were absorbed for 5 min before emission, and the emission time was 20 min. The results are shown in Figure 3.

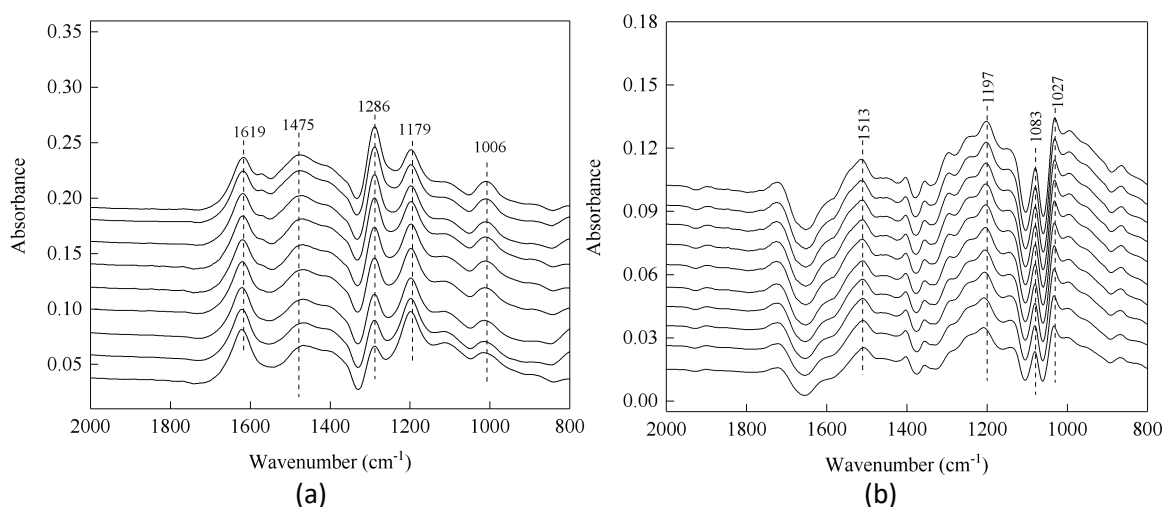


Figure 3: DRIFTS spectra of surface products as a function of reaction time during the reaction of Fe₂O₃ particle surfaces with NO (1000 ppm)/O₂ (10%); (a) dry Fe₂O₃; (b) humid Fe₂O₃.

Figure 3 (a) shows the DRIFTS spectra of the products after NO (1000 ppm) / O₂ (10%) / N₂ reaction on the dried Fe₂O₃ powder surface. There were four obvious absorption peaks: at 1179cm⁻¹, 1286cm⁻¹, 1475cm⁻¹, and 1619cm⁻¹, which increased with time. Among them, there were two peaks near 1179cm⁻¹ and 1286cm⁻¹, which belong to monodentate nitrite [Fe-O-N-O] and monodentate nitrate [Fe-O-NO₂], being the V1 vibration of nitrite and the V3 vibration of nitrate. The lower intensity peaks at 1475cm⁻¹ and 1619cm⁻¹ belong to monodentate nitrate [Fe-O-NO₂] and bridge nitrate [(Fe-O)₂=NO], which are the V3 vibrations of nitrate. The variation in the intensity of different absorption peaks also indicates that nitrate species formed on the surface of the metal oxides via the lattice oxygen reaction of nitrite and the Fe₂O₃ surface[15]. In the presence of oxygen, NO reacts with O₂ to form NO₂, which helps to enhance the adsorption capacity of nitrate. At the same time, the presence of O₂ can also promote the transformation of nitrite species to nitrate species. Therefore, compared with section 3.1.1, nitrate is more easily formed after Fe₂O₃ adsorbs NO₂ in the presence of oxygen.

Figure 3 (b) shows the DRIFTS spectra of the products after NO (1000 ppm) / O₂ (10%) / N₂ reaction on the wet Fe₂O₃ powder surface. The intensity of absorption peak decreased in a humid environment, and the strongest absorption peak appeared at 1027cm⁻¹.

3.2. Adsorption State of SO₂ on the Fe₂O₃ Surface

The adsorption state of SO₂ on the Fe₂O₃ surface was studied under two working conditions: aerobic and anaerobic conditions, namely SO₂ (500 ppm) and SO₂ (500 ppm) / O₂ (10%) / N₂. The results are presented below.

3.2.1. Change of SO₂ (500 ppm) / N₂ on the Fe₂O₃ Surface

The dried Fe₂O₃ sample was placed in the diffuse reflection reaction tank and was then passed into SO₂ (500 ppm)/N₂ for adsorption. The flow rate was 80 ml / min, the spectra were emitted after 5 min of adsorption, and the emission time was 20 min. The results are shown in Figure 4.

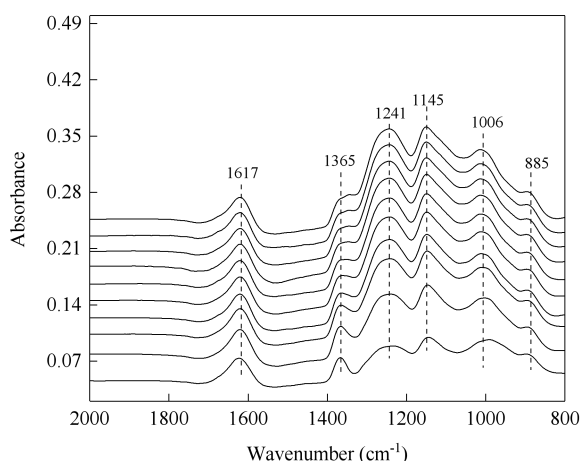


Figure 4: DRIFTS spectra of surface products as a function of reaction time during the reaction of Fe₂O₃ particle surfaces with SO₂ (500 ppm).

The peak position of the heterogeneous SO₂ reaction was mainly concentrated in the range of 1400-1000cm⁻¹ (Figure 4), and the peak intensity increased. Strong absorption peaks were observed at 1066 cm⁻¹, 1145 cm⁻¹, and 1241cm⁻¹, belonging to the V3 vibration. The symmetrical stretching vibration peak of sulfate appeared at 885 cm⁻¹, with weak infrared absorption, and a weak absorption peak occurred at 1365 cm⁻¹, indicating that a small amount of sulfite was produced in

the reaction process. The above absorption peaks are basically consistent with the results of Nanaykkara et al.[15]. In addition, at 1617 cm⁻¹, there was an absorption peak of NO in the gas phase, which may be due to the mixing of NO in the diffuse reflection cell. The absorption peaks with wave numbers of 1365cm⁻¹, 1241cm⁻¹, and 1145cm⁻¹ belong to the condensed state of sulfate, bidentate sulfate, and bridge sulfate, respectively [16]. The results show that SO₂ can promote the adsorption and reaction of Fe₂O₃.

3.2.2. Change of SO₂ (500 ppm) / N₂ on the Fe₂O₃ Surface

The dried Fe₂O₃ samples were placed in the diffuse reflection reaction tank and then supplied with SO₂ (500 ppm) / O₂ (10%) / N₂ for adsorption at a flow rate of 80 ml / min. with either dry or wet Fe₂O₃ samples. The samples were adsorbed for 5 min before emission, and the emission time was 20 min. The results are shown in Figure 5.

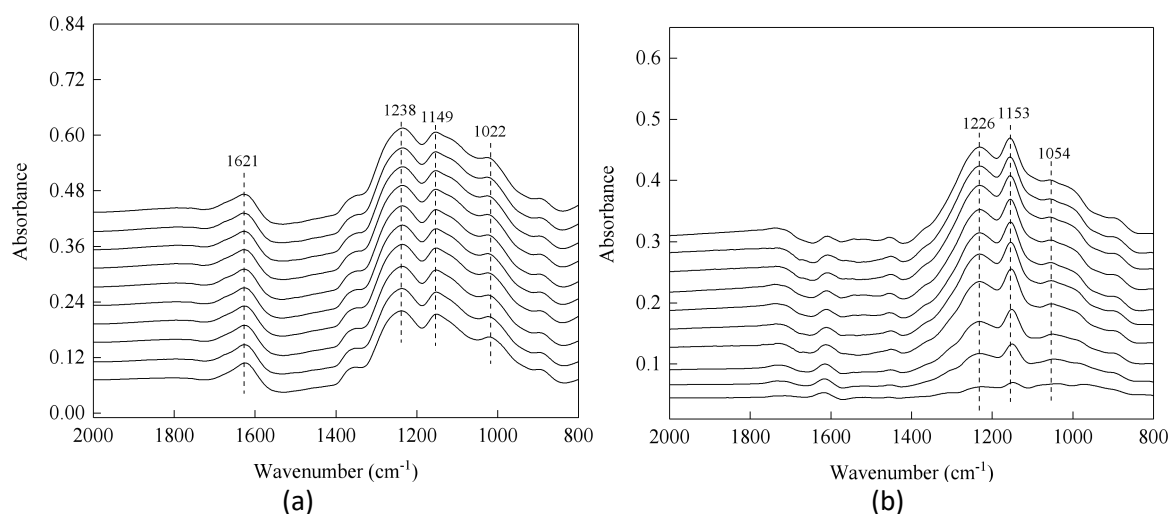


Figure 5: DRIFTS spectra of surface products as a function of reaction time during the reaction of Fe₂O₃ particle surfaces with SO₂ (500 ppm) / O₂ (10%); (a) dry Fe₂O₃; (b) humid Fe₂O₃.

As shown in Figure 5 (a), under dry conditions, strong absorption peaks appeared at 1022cm⁻¹, 1149.36 cm⁻¹, and 1238 cm⁻¹, which are the bidentate coordination of sulfate and belong to the V3 vibration[16]. With the increase in adsorption time, the intensity of the three absorption peaks was close to the saturation state, which indicates that the adsorption of SO₂ on the Fe₂O₃ surface was obviously enhanced, and that the formation of sulfate on the Fe₂O₃ surface was promoted. However, in a humid environment, as shown in Fig. 5 (b), the absorption peaks at 1054cm⁻¹, 1153cm⁻¹, and 1226cm⁻¹ belong to the antisymmetric stretching vibration peak of sulfate[17]. Under relatively humid conditions, the absorption peaks gradually increased with an increase in time, indicating that the reaction of SO₂ on the Fe₂O₃ surface was affected by these conditions.

3.3. Adsorption state of NO and SO₂ on the Fe₂O₃ Surface

The heterogeneous transformation of SO₂ on atmospheric particulates must be affected by NO₂ itself and its pre-adsorbed products. Previous field studies not only proved that sulfate mixed with nitrate and mine dust, but also that NO₂ played an important role in the surface transformation and heterogeneous reaction of SO₂[18]. To observe the synergistic effect of NO and SO₂ adsorption on the Fe₂O₃ surface, dry Fe₂O₃ samples were placed in a diffuse reflectance cell, and NO (1000 ppm) / SO₂ (500 ppm) / O₂ (10%) / N₂ was introduced. The flow rate was 80 ml / min, the adsorption time was 5 min, and the emission time was 20 min. The results are shown in Figure 6.

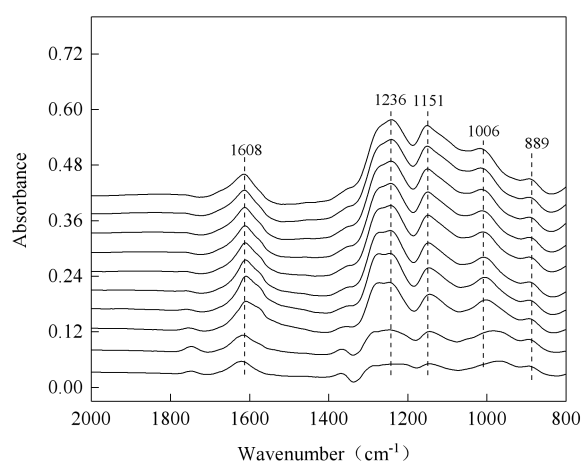
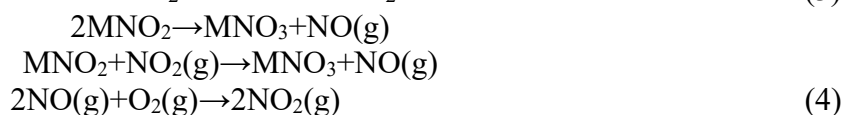
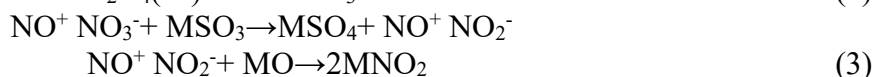


Figure 5: DRIFTS spectra of surface products as a function of reaction time during the reaction of Fe₂O₃ particle surfaces with SO₂ (500 ppm) /O₂ (10%)/NO (1000 ppm).

As shown in Figure 6, the symmetrical stretching vibration peak of sulfate appeared at 889 cm⁻¹, and the infrared absorption was weak. The peak at 1147cm⁻¹ is the antisymmetric stretching vibration peak of sulfate, with strong infrared absorption, belonging to monodentate nitrate (V1) at 1010cm⁻¹. This peak gradually decreased with time. Single and double tooth coordinations of nitrate were generated at 1236 cm⁻¹ and 1286cm⁻¹, belonging to sulfuric acid. The V3 vibration of salt is the symmetrical stretching vibration peak of nitrate; it belongs to bridge nitrate at 1608cm⁻¹[19]. The results showed that the adsorption of nitrate contributed to the formation of sulfate.

In conclusion, the reaction mechanism of the synergistic effect of SO₂ and NO_x on the surface of Fe₂O₃ metal particles is analyzed as follows: firstly, gaseous NO₂ and SO₂ are adsorbed on the surface of Fe₂O₃ to form adsorbed NO₂(ad) and sulfite respectively, and the dimer of NO₂ (ad) is N₂O₄(ad). Because the Henry's law coefficient of N₂O₄ in water is about two orders of magnitude larger than that of NO₂ [20], the accumulation of N₂O₄ is more likely to occur when there is water on the surface of metal oxides. However, the pre adsorbed water can not lead to the formation of N₂O₄ on Fe₂O₃. Therefore, the formation of N₂O₄ may be related to the surface sulfur (IV). In addition, O₂ also promoted the formation of N₂O₄ under the condition of oxygen enrichment. Therefore, N₂O₄ autoionizes to form NO⁺NO₃⁻, which oxidizes sulfite to sulfate, while NO⁺NO₃⁻ are reduced to nitrite. Finally, nitrite is converted to nitrate and gaseous no, and the released no is oxidized to NO₂ and enters the next reaction cycle. The reaction process is as follows:



4. Conclusions

Reaction gases were introduced into a dry environment without oxygen, and into an aerobic environment under dry and wet conditions, respectively. Micro reactions on the surface of Fe₂O₃

were observed, and adsorbed sulfates and nitrates with different coordination forms were studied. The results showed that NO, SO₂, and mixed NO / SO₂ gas reacted with oxygen vacancies and the coordinated oxygen of Fe³⁺, respectively, to finally adsorb on the surface of Fe₂O₃ in the form of different nitrates and sulfates. The adsorption of water on the surface, the adsorption of nitrate itself, and the catalytic reduction of Fe₂O₃ metal particles affected the heterogeneous oxidation of SO₂. The above results indicate that in addition to a strict management, technical progress, end treatment, and other means, we also need to strengthen the control of the metal content in oil products at the source, so as to improve the prevention and control of air pollution in the future.

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