Calculation and analysis of the amount of secondary component products of NOx and SO2 on metal oxide surface based on Drifts simulation: A case study of vehicle exhausts emission

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Abstract. In this paper, the micro reactions of SO2 and NOx in the metal oxides (Fe2O3, MgO, MnO2, Al2O3, ZnO, CuO, SiO2 and Cr2O3) from vehicle exhaust are studied by diffuse reflectance infrared spectroscopy (DRIFTS). The amount of secondary component in PM2.5 is analyzed by observing the synergistic or antagonistic effects of different gases on the surface of different metal oxides. The results show that when SO2 and NO2 coexist, the formation of sulfate is greatly promoted on the surface of Fe2O3 metal particles, and the intermediate sulfite is formed at the initial stage and then rapidly oxidized to sulfate. Under the condition of oxygen enrichment, the total species content of secondary components of fine particles formed on the surface of metal oxides is Cr2O3 > Fe2O3 > MgO > MnO2 > Al2O3 > ZnO > CuO > SiO2. because Cr2O3 has a strong ability to adsorb and activate acid gas, so the content of surface species generated in the micro reaction is more than that of other metal oxides; the metal oxides containing iron, magnesium and manganese can more effectively convert SO2 into sulfate in the presence of NOx, but the sulfate generated on the surface of Cr2O3, CuO and Al2O3 decreases, which leads to the difference of metal oxide activity. This result has a certain guiding significance for the reaction of SO2 and NOx to metal oxides emitted by motor vehicles in the atmosphere.

1. Introduction
Nowadays, the harm of PM2.5 has aroused widespread concern of the government and the public, and motor vehicle emissions are one of the main causes of air pollution. Serious haze events are usually caused by composite pollutants, mainly from coal combustion and motor vehicle emissions. With the aggravation of air pollution and the impact on urban air quality, the air pollution caused by motor vehicle emissions has become increasingly prominent [1]. The gaseous pollutants emitted by motor vehicles include nitrogen oxides (NOx), volatile organic compounds (VOCs), carbon monoxide (CO) and carbon
dioxide (CO$_2$), as well as carbon particles in the form of black carbon (BC) and organic carbon (OC). These gaseous pollutants and carbon particles cause public health problems [2]. In recent years, from the perspective of the number of vehicle (machine) types, the number of urban motor vehicles in China continues to grow at a high speed. The total emissions of CO and PM from motor vehicles exceeded 0.36 billion in 2018, accounting for 48.90% of the total emissions from motor vehicles in China. The NOx emission of diesel vehicles exceeds 80% of the total vehicle emission, and the PM emission exceeds 90%, which leads to the increasing emission of vehicle exhaust and affects the increase of air pollutant emission, which is an important part of PM$_{2.5}$ [3]. In addition to NOx and VOCs emission as the important premise of PM$_{2.5}$, motor vehicles also contain some metal elements from additives and lubricants, which also participate in the formation of air pollutants to a certain extent. Lin [4, 5] and others analyzed the chemical composition and metal element concentration of PM$_{2.5}$ in vehicle exhaust by ICP-OES. The results showed that the content of metal elements in PM$_{2.5}$ was in the order of Ca > Al > Zn > K > Fe > Mg > Cr. This result is helpful to further study the influence of vehicle exhaust on the chemical composition in ambient air and metal element concentration in atmosphere. Soot in the atmosphere is easy to absorb light, which is considered to be the main reason for reducing atmospheric visibility, and also the main contribution source of PM$_{2.5}$ formation. At the same time, some scholars [6] believe that soot absorption in diesel particulate matter reduces visibility, and nitrate and sulfate species are formed on the surface of particulate matter, which promotes the formation of PM$_{2.5}$.

In practical research, single component particles are often used to simulate the reaction between a certain component of particles and trace gases in the actual atmospheric environment. The existing research results show [6-10] that the reaction process between gaseous pollutants and particulates changes the chemical composition and surface characteristics of particulates, increases the hygroscopicity of particulates, increases the concentration of particulates, and has obvious extinction effect, which reduces the atmospheric visibility and promotes the formation of PM$_{2.5}$. It can be seen that the micro reaction between gaseous pollutants and metal particles plays a significant role in the formation of PM$_{2.5}$ secondary components. However, in the standards of vehicle gasoline (GB 17930-2016) and vehicle diesel (GB 19147-2016), only the quality indexes and experimental methods of iron and manganese are mentioned in the technical requirements and experimental methods, but the quality indexes and experimental methods of other metals are not mentioned, which indicates that the trace metal elements contained in diesel vehicles and gasoline vehicles have not been paid attention to. Therefore, in this paper, we use drifts to analyze the micro phenomena of NO, NO$_2$, SO$_2$ gas adsorption, decomposition and combination on the surface of the above metal oxides under oxygen enriched conditions, and select eight kinds of metals such as Fe, Al, Cu, Mn, Zn, Mg, Si and Cr as the research objects, so as to analyze whether the chemical reactions between different reaction gases and metal particles have synergistic or antagonistic effects Therefore, the contribution of pollutants emitted by motor vehicles to the formation of PM$_{2.5}$ secondary components should be analyzed to provide a theoretical basis for the prevention and control of air pollution.

2. Experimental methods and equipment

2.1. Experimental facility
According to the research of scholars, in addition to C, the metal parts of particulate matter in diesel and gasoline vehicles mainly include Fe, Zn, Cu, Si, Cr, Al, Mn, Mg and other metal elements [15]. Although different oil products are used, their chemical properties are very similar, so it is feasible to use drifts for heterogeneous reaction simulation research. Because diffuse reflectance infrared spectroscopy can detect the surface changes of particles very sensitively, this method has been widely used in the fields of catalytic oxidation and photochemistry [16]. Therefore, this paper uses drifts method to analyze the surface species of particles.
Figure 1. Diffuse reflection infrared reaction test device and gas path diagram

As shown in Figure 1, the diffuse reflectance infrared instrument is connected with an external gas distribution system, including four gases: N₂, O₂, NO and SO₂. The four gases are regulated by mass flow controller (MFCs) according to the test requirements before entering the diffuse reflectance infrared spectrometer. The main functions of each gas in the gas distribution system are: N₂ is used to purge the instrument channel before the test to keep the pipeline clean; in addition, it is also used as dilution gas; reaction gases no and SO₂ are the gases participating in the reaction; O₂ is the mixed gas with different oxygen content after being diluted by N₂.

2.2. Experimental materials and instruments

| The gas | Specification | Manufacturer |
|---------|---------------|-------------|
| O₂      | 99.9997%      | Fulian Technology Gas (Kunshan) Co., Ltd |
| N₂      | 99.99%        | Fulian Technology Gas (Kunshan) Co., Ltd |
| NO      | 99.99%        | Fulian Technology Gas (Kunshan) Co., Ltd |
| SO₂     | 99.99%        | Fulian Technology Gas (Kunshan) Co., Ltd |

Fe₂O₃, Al₂O₃, CuO, MgO, MnO₂, SiO₂, ZnO and Cr₂O₃ powder: the analytical purity (AR) selected in the laboratory, Sinopharm Chemical Reagent Co., Ltd., is the powder without pretreatment, and its relative humidity is the same as that in the atmosphere.

Fourier transform infrared spectrometer (FT-IR) and diffuse reflectance accessory: Fourier transform infrared spectrometer (EQUINOX-55, Bruker company, Germany). The test was carried out on nexus 670 diffuse reflectance infrared analysis device produced by Nicole company. The spectral range is 650-4000 cm⁻¹, the resolution is 4 cm⁻¹, and the scanning time is 256. Before the heterogeneous reaction, all samples were ground into powder and filled in the in-situ cell at room temperature and atmospheric pressure. The composition and flow rate of the reaction gas are controlled by the mass flowmeter, and the total flow rate is 80 ml / min. During the experiment, O₂ and N₂ were introduced into the reaction chamber through a gas dryer. NO (1000 ppm, NO₂ / N₂) and SO₂ (500 ppm, SO₂ / N₂) were used as reaction gases.

3. Results and discussion

3.1. Reaction process of nitrate and sulfate formation on Fe₂O₃ surface exposed to different gases

According to the infrared spectra of no, NO₂ and SO₂ on the surface of Fe₂O₃ particles (Figure 2), the integral evolution process of the infrared peaks of nitrate and sulfate is obtained, as shown in Figure 3.
Figure 2. DRIFTS diagram of Fe₂O₃ surface exposed to different gases: (a) NO(1000ppm); (b) NO(1000ppm)/O₂(10%); (c) SO₂(500ppm)/O₂(10%); (d) NO(1000ppm)/O₂(10%)/SO₂(500ppm)

It can be seen from Figure 2 (a) and Figure 3 (a) that different coordination forms of nitrate are formed on the surface of Fe₂O₃ particles by NO. It can be seen that the adsorbed nitrate is the main product of heterogeneous absorption of NOx on the surface of Fe₂O₃ particles. However, after 10 minutes of reaction, with the increase of reaction time, the infrared peak integral area of nitrate tends to be saturated, and gradually stabilized after 20 minutes. At the same time, when O₂ (10%) is added, the time of nitrate formation increases. It can be seen that the nitrate content increases with the increase of reaction time (as shown in Fig. 2 (b) and Fig. 3 (b)), and tends to be stable after 40 min. Therefore, the introduction of oxygen promotes the formation of nitrate in the micro reaction of NOx and Fe₂O₃ particles.

Figure 3. Evolution of the integral area of infrared peaks on Fe₂O₃ surface exposed to different gases: (a) NO(1000ppm); (b) NO(1000ppm)/O₂(10%); (c) SO₂(500ppm)/O₂(10%); (d) NO(1000ppm)/O₂(10%)/SO₂(500ppm)
Through the micro reaction of single gas SO$_2$ on the surface of Fe$_2$O$_3$ particles, different coordination forms of sulfate are generated in Figure 2 (c) with the wave number of 889-1998 cm$^{-1}$ and 1151 cm$^{-1}$, which are respectively condensed, bidentate sulfate and Bridge sulfate in sulfuric acid Basin [17]. With the increase of reaction time, the formation content of sulfate fluctuates (as shown in Figure 3 (c)), and tends to be stable after 40min. For Fig. 2 (d) and Figure 3 (d), when SO$_2$, no and O$_2$ flow into the reaction tank at the same time, a very obvious infrared peak appears. It can be seen from the figure that the absorption peaks of nitrate and sulfate gradually increase with time. By comparison, the nitrate content generated by the reaction of single gas no and Fe$_2$O$_3$ metal particles is less than that generated by SO$_2$ and no, which indicates that the introduction of SO$_2$ promotes the increase of nitrate content, and that SO$_2$ can be finally oxidized to sulfate in the presence of NO$_2$, which indicates that NO$_2$ also promotes the oxidation of SO$_2$, in which there is intermediate Compound N$_2$O$_4$ was used as oxidant. The formula is as follows [18]:

\[
\begin{align*}
2\text{NO}_2 & \leftrightarrow \text{N}_2\text{O}_4, \\
\text{N}_2\text{O}_4+\text{M-O} & \rightarrow \text{MNO}_2+\text{MNO}_3 \\
\text{N}_2\text{O}_4+\text{S (IV)} & \rightarrow \text{MNO}_2+\text{S (IV)} \\
\text{MNO}_2+\text{NO}+\text{O}_2 & \rightarrow \text{MNO}_3
\end{align*}
\]

Therefore, when SO$_2$ and NO$_2$ coexist, it can be seen that the formation of sulfate is greatly promoted on the surface of Fe$_2$O$_3$ metal particles, and the intermediate sulfite is formed at the initial stage, and then quickly oxidized to sulfate. It can be concluded that SO$_2$ can be oxidized to sulfate species in the presence of NO$_2$ when heterogeneous reaction takes place on the surface of the studied oxides. In the reaction system of metal oxides, iron containing metal oxide particles in the presence of NOx and SO$_2$ may more effectively convert SO$_2$ into sulfate, which indicates that the synergistic effect of NOx and SO$_2$ promotes the formation of sulfate.

3.2. The reaction process of nitrate and sulfate on the surface of other metal oxides exposed to mixed gases

After studying the heterogeneous reaction of single gas and mixed gas on the surface of Fe$_2$O$_3$ particles, and continuing to study the heterogeneous reaction of reaction gas on the surface of other metal oxides, the reactions occurred on the surface of Al$_2$O$_3$, CuO, MgO, MnO$_2$, SiO$_2$, ZnO and Cr$_2$O$_3$. The heterogeneous reactions of no and SO$_2$ on the surface of metal particles were mainly carried out including the reaction of coexistence of SO$_2$ and NO.
Figure 4. Integral area evolution of infrared peaks of mixed gases (NOx, SO2) on the surface of other metal oxides

The reaction conditions are the same as that of Fe2O3, as shown in Figure 4, which is the evolution process of infrared integral area of sulfate and nitrate generated by the reaction on the surface of other metal oxides with mixed gases (NO (1000ppm), SO2 (500ppm) and O2 (10%)) (the analysis conditions of the following mixed gases are mainly NO (1000ppm), SO2 (500ppm) and O2 (10%). When NOx and SO2 are exposed to the diffuse reflection cell, because the gas phase NOx and SO2 may adhere to the surface active sites of alumina and magnesia particles and form the adsorption phase NOx and SO2, the two types of adsorption phase NOx and SO2 can react with the surface OH substances to form NO3- / NO2- and SO3- / SO4-, NOx and SO2 promotes the formation of sulfate on metal oxides [19], indicating that the reaction pathways of SO2 are different in the presence of NOx.

For other metal oxides, the content of nitrate formed by reaction is much higher than that of sulfate. Under oxygen enriched conditions, the presence of SO2 significantly promotes the formation of nitrate species on the surface of metal oxides, indicating that enhanced atmospheric oxidation plays an important role in the reaction process. In Fig. 3 (g), the main reason why the reaction time of Cr2O3 is set at 220min is that Cr2O3 has a strong ability to adsorb and activate acid gas [20]. According to the experimental observation, the reaction time is 120min And the heterogeneous reaction is more intense than that of other metal oxides. The results show that the surface properties of metal oxides play an important role in the synergistic effect between SO2 and NOx, which has a certain guiding significance for the atmospheric reaction of SO2 and NOx on metal oxides emitted by motor vehicles. It is found that nitrate and sulfate are the main causes of serious haze pollution in China. With the increase of dust, serious pollution events can be attributed to the formation of new particles.
As shown in Figure 5, the infrared peak area of mixed gas reaction on the surface of different metal particles is compared. Under the mixed gas reaction, the infrared peak area of nitrate generated on the surface of Cr$_2$O$_3$ is the largest, followed by Fe$_2$O$_3$, MgO, MnO$_2$, etc. The synergistic effect of NO and SO$_2$ promoted the formation of sulfate and nitrate. Under the condition of oxygen enrichment, the total species content of secondary components of fine particles formed on the surface of metal oxides is Cr$_2$O$_3$ > Fe$_2$O$_3$ > MgO > MnO$_2$ > Al$_2$O$_3$ > ZnO > CuO > SiO$_2$. Among them, Fe$_2$O$_3$, Al$_2$O$_3$, MnO$_2$ and MgO have more sulfate formation, almost no sulfite formation, which indicates that NOx and SO$_2$ have no obvious promoting effect on the formation of sulfite, but have obvious promoting effect on the formation of sulfate, so it is found that the adsorption of SO$_2$ and NOx promote each other, which indicates that the micro reaction in the diffuse reflection cell can reproduce the synergistic effect.

3.3. Comparison of infrared peak areas generated by the reaction of mixed gas and single gas on the surface of metal particles

In the previous study, the micro reaction of single gas and mixed gas on the surface of metal oxide is discussed. To further compare species generated by single gas and mixed gas on the surface of metal oxide, Figure 6 shows the infrared integral area comparison of the reaction of mixed gas and no to nitrate on the surface of metal oxide.

The results show that the infrared peak area of nitrate formed by Cr$_2$O$_3$ is the largest under oxygen enriched condition, indicating that the reaction of different gases on the surface of Cr$_2$O$_3$ particles is more intense, followed by Fe$_2$O$_3$, MgO and MnO$_2$. In the reaction gas, the reaction of nitrate formation on the surface of Fe$_2$O$_3$, MgO, ZnO and Cr$_2$O$_3$ by mixed gas is more intense than that by single gas no, which indicates that the introduction of SO$_2$ promotes the formation rate of nitrate. After the addition of SO$_2$, nitrate formation is obvious on the surface of Fe$_2$O$_3$, MgO, ZnO and Cr$_2$O$_3$, which is due to the different adsorption sites on the oxide surface and the synergistic effect. However, the reaction of single
gas on the surface of other metal oxides such as Al2O3 and CuO is stronger than that of mixed gas, which indicates that the reaction of mixed gas on the surface of these metal oxides has antagonistic effect and hinders the formation of nitrate.

![Figure 7](image)

**Figure 7.** Comparison of infrared integral area of sulfate formed by reaction of mixed gas and SO2 on metal oxide surface

Similarly, Figure 7 compares the infrared integral area of sulfate formed by the reaction of mixed gas and SO2 on the surface of metal oxide. The results show that the synergistic or antagonistic effects of SO2 and NOx on different metal oxides indicate that these metal oxides play different roles in the conversion of SO2 and NOx in atmospheric system. It is found that in the absence of NOx, the sulfate content decreases in the order of Cr2O3 > Fe2O3 > MnO2 > MgO > Al2O3 > CuO. When coexisting with NOx, the reaction of sulfate on Fe2O3, Al2O3, MnO2 and MgO surface is stronger than that on SO2 surface, which indicates that metal particles containing iron, magnesium and manganese may convert SO2 to sulfate more effectively in the presence of NOx. However, the sulfate produced by Cr2O3, CuO and Al2O3 is reduced, and the difference of metal oxide activity is caused by the change of metal surface properties [21]. Therefore, before further establishing the relationship between metal oxides and the transformation of sulfur and nitrogen species, we should consider the influence of oxygen species, the acid-base properties of surface hydroxyl groups, and the different mixed forms of metal particles.

4. Conclusion

Under the same conditions, the total species content of secondary components of fine particles formed on the surface of metal oxides is Cr2O3 > Fe2O3 > MgO > MnO2 > Al2O3 > ZnO > CuO > SiO2. Because Cr2O3 has a strong ability to adsorb and activate acid gas, more surface species are generated in the micro reaction than other metal oxides; metal oxides containing iron, magnesium and manganese can convert SO2 to sulfate more effectively in the presence of NOx, but the sulfate generated by Cr2O3, CuO and Al2O3 is reduced. Therefore, in the atmospheric environment, the reaction between metal oxides emitted by motor vehicles and NOx and SO2 makes a significant contribution to nitrate and sulfate in the atmosphere. Therefore, in the atmospheric environment, the reaction between metal oxides emitted by motor vehicles and NOx and SO2 makes a significant contribution to nitrate and sulfate in the atmosphere.

References

[1] Kim Oanh N T, Upadhyaya N, Zhuang Y H, et al. Particulate air pollution in six Asian cities: Spatial and temporal distributions, and associated sources[J]. Atmospheric Environment, 2006, 40(18): 3367-3380.

[2] Jung H J, Kittelson D B, Zacharich M R. The influence of a cerium additive on ultra-find diesel particle emissions and kinetics of oxidation Combustion [J]. 2005, 142(2): 276-288.

[3] Ministry of ecological environment of the people's Republic of China. China Mobile Source Management Annual Report [N], 2020.

[4] Yuan-Chung Lin, Ya-Ching Li, Kassian T.T. Amesho, et al. Chemical characterization of PM2.5 emissions and atmospheric metallic element concentrations in PM2.5 emitted from mobile source gasoline-fueled vehicles [J]. Science of the Total Environment, 2020, 739: 139942.
[5] Thomas W, Kirchstetter, Jeffery Aguiara, et al. Black carbon concentrations and diesel vehicle emission factors derived from coefficient of haze measurement in California: 1967-2003[J]. Atmospheric Environment, 2008, 42(3): 480-491.

[6] Wei Liu, WuGao Zhang, Zhu Lei, et al. Characteristics of ultrafine particle from a compression-ignition engine fueled with low sulfur diesel [J]. Chinese Science Bulletin, 2009, 54(23): 4411-4417.

[7] S. A. Kukushkin, A. V. Osipov. Drift mechanism of mass transfer on heterogeneous reaction in crystalline silicon substrate[J]. Physica B: Condensed Matter, 2017, 512: 26-31.

[8] Underwood G M, Miller T M, Grassian V H, et al. Transmission FT-IR and Knudsen Cell Study of the Heterogeneous Reactivity of Gaseous Nitrogen Dioxide on Mineral Oxide Particles[J]. The Journal of Physical Chemistry A, 1999, 103(31): 6184-6190.

[9] Goodman A L, Underwood G M, Grassian V H et al. Heterogeneous Reaction of NO2: Characterization of Gas-Phase and Adsorbed Products from the Reaction, 2NO2(g) + H2O(a) → HONO(g) + HNO3(a) on Hydrated Silica Particles[J]. The Journal of Physical Chemistry A, 1999, 103(36): 7217-7223.

[10] Shahid Saqlain, Byeong Jun Cha, Soong Yeon Kim, et al. Impact of humidity on the removal of volatile organic compounds over Fe loaded TiO2 under visible light irradiation: Insight into photocatalysis mechanism by operando DRIFTS[J]. Materials today communication, 2021, 26: 102119.

[11] Bingye Xu, Tong Zhu, Xiaoyan Tang, et al. Heterogeneous reaction of formaldehyde on the surface of titanium dioxide particles[J]. Chinese Science: Chemistry, 2010, 40(12): 17571764.

[12] Chang Liu, Qingxin Ma, Yongchun Liu, et al. Synergistic reaction between SO2 and NO2 on mineral oxides: a potential formation pathway of sulfate aerosol[J]. Physical Chemistry Chemical Physics, 2012,14: 1668-1676.

[13] Chuan Yu, Ze Wang, Qingxin Ma, et al. Measurement of heterogeneous uptake of NO2 on inorganic particles, sea water and urban grime[J]. Journal of Environmental Sciences, 2021, 106: 124-135.

[14] Chengtian Du, Lingdong Kong, Assiya Zhazhazhova, et al. Impact of heterogeneous uptake of nitrogen dioxide on the conversion of acetaldehyde on gamma-alumina in the absence and presence of simulated solar irradiation[J]. Atmospheric Environment, 2018, 187: 282-291.

[15] Yingjir Li. Effect of Micro-Components from Diesel Particulate Matter on Haze [J]. Journal of Shanghai University of engineering and technology, 2016, 30(04): 290-293.

[16] Yan Qiu. The Principle and Application Research of Diffuse Reflectance Spectrum[D]. Tongji University, 2007.

[17] Stephan J.Hug. In Situ Fourier Transform Infrared Measurements of Sulfate Adsorption on Hematite in Aqueous Solutions[J]. Journal of Colloid and Interface Science, 1997, 188(02): 415-422.

[18] Qingxin Ma, Yongchun Liu, and Hong He. Synergistic Effect between NO2 and SO2 in Their Adsorption and Reaction on γ-Alumina [J]. The Journal of Physical Chemistry, 2008, 112(29): 6630-6635.

[19] Weiwei Yang, Jinzhu Ma, Yongchun Liu. Synergistic formation of sulfate and ammonium resulting from reaction between SO2 and NH3 on typical mineral dust[J]. Physical Chemistry Chemical Physics, 2015, 18(2): 956-964.

[20] S. N. Hernández Guiance, I. D. Coria, I. M. Irurzun, et al. Experimental determination of the activation energies of CH4, SO2 and O2 reactions on Cr2O3/ γ-Al2O3[J]. Chemical Physics Letters, 2016, 660(01): 123-126.

[21] Chen Liu. Surfactant-Enhanced Metal Oxide Catalyzed Ozone Oxidation of Ammonia Nitrogen Water [D]. Jiangxi University of science and technology, 2019.