Impact of single metal oxide and coal ash on secondary ultrafine particle generation through SO$_2$ and NO$_2$ heterogeneous reaction

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ABSTRACT: Particulate matter research is of great significance in solving atmospheric environment problems. The heterogeneous reaction of mixed gas on different mineral oxides and coal ash was studied based on a laboratory-built aerosol generating reactor. The product formed on particles was investigated by ion chromatography (IC). SO$_2$ and NO$_2$ could react on oxides to form secondary particles and the order of reactivity of mineral oxides under laboratory reaction conditions is: Al$_2$O$_3$>MgO>CaO>>SiO$_2$, Fe$_2$O$_3$. NO$_2$ has a synergistic effect on the heterogeneous reaction of SO$_2$ on Al$_2$O$_3$ in the presence of O$_2$. The synergistic effect of SO$_2$ and NO$_2$ on Al$_2$O$_3$ is further enhanced in the case of high relative humidity (RH) and in the presence of NH$_3$. The reaction on Al$_2$O$_3$ under different gas concentration ratios is compared, and it is identified that SO$_2$ and NO$_2$ concentrations make an effect on aerosol production. The heterogeneous reactions of SO$_2$ and NO$_2$ on various coal ash are different. The order of reactivity of the three coal ashes is WH>MHU>Centennial. The secondary particulate matter formed on coal ash is higher than that on single metal oxide.

Key words: SO$_2$, NO$_2$, NH$_3$, Coal ash, Secondary ultrafine particle, Ion chromatography

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1. Introduction

With the continuous advancement of industrialization, more and more factories appear and have given rise to serious air pollution problems. The main cause of air pollution is atmospheric particulate matter. Its sources are complex including natural sources (sand, sea salt, H2S, NH3, NOx, HC, etc.) and anthropogenic sources (human activities produce sand, industrial emissions, secondary particles formed by the conversion of NOx, SO2, HC, etc.). Atmospheric particulate matter consists of primary and secondary particulate matter. Particles which directly given off into the atmosphere from energy-consuming places such as factories, vehicles (cars), and power plants are primary particulate matter. Secondary particulate matter (such as sulfate, nitrate, ammonium salts, etc.) is produced by the chemical reaction between some pollutant components in the atmosphere (SO2, NOx, hydrocarbons) or between these components and atmospheric components (such as oxygen). Atmospheric particulate matter is harmful to the human body. Small-size particles can be directly inhaled by the human body and deposited in the bronchi and lungs. Particles with a size of between 0.1 and 2.5 μm have the greatest impact on human health and with the aerodynamic equivalent diameter of 2.5 μm or less is PM2.5. PM2.5 with a complex chemical composition is the main carrier of pollutants released by human activities. The secondary inorganic particulate matter occupies a large proportion of PM2.5 components, and its main constituents include sulfates, nitrates, and ammonium salts. The secondary inorganic aerosols exert an enormous function of the formation of haze weather[1, 2].

Studying the formation process of secondary particles is crucial to solving air pollution. The three research methods of atmospheric chemistry (numerical simulation, external field observation and laboratory research) all show the momentous effect of heterogeneous reactions in atmospheric chemical reactions, which feature in the conversion of tropospheric contaminating gas and the creative of secondary aerosols[3-6]. Heterogeneous reactions alter surface properties and chemical composition of particulate matter[7-12]. This has a considerable influence on human health, ecology and climate system. Therefore, studying the heterogeneous reaction heterogeneity of aerosols count for a great deal. The correlation coefficient between SO4^2- and SO2 concentration in PM2.5 in Shanghai is large, indicating a strong correlation between the two. It can be speculated that SO2 emissions are a crucial source of SO4^2- [13]. The model study found that there is a problem of the underestimation of sulfate in atmospheric aerosols. The heterogeneous reaction on mineral particles is considered a vital process of sulfate generation, and the mechanism of SO2 reaction to bring about sulfate on various kinds of mineral particles is distinct[14]. SO2 reacts on the surface of mineral oxides and forms sulfite only on basic oxygen vacancies or hydroxyl sites[15, 16]. Related studies have pointed out that SO2 is adsorbed on the exterior of particles in the process of the heterogeneous transformation of some mineral oxide particles, and then the produced sulfite is swiftly oxidized by ozone to form sulfate[17,18]. Laboratory researches have shown that SO2 is not easy to form sulfate under air atmosphere,
but the coexisting O$_3$ can accelerate the conversion of SO$_2$ to sulfate[15, 17, 19]. Moreover, lowering the reaction temperature contributes to the creation of sulfate[20]. It is found that SO$_2$ can be directly converted into SO$_4^{2-}$ on Fe$_2$O$_3$, due to the oxidation of Fe (III) [21]. It has also been pointed out that most of the sulfates are formed by heterogeneous oxidation when RH is greater than 75%[22]. The sulfur conversion rates increased with the growth of O$_3$ concentration and relative humidity (RH) when studying the conversion of sulfate and nitrate in urban atmosphere[23].

The reaction rate of NO$_2$ on particles is slow in dry condition[24]. At this point, the impact of heterogeneous reactions on atmospheric chemical reactions is not obvious. It is found through infrared spectroscopy that NO$_2$ can react on the super-crust of mineral oxides to form nitrates under dry conditions, which are dissolved in water film on the surface of mineral oxides during water adsorption to bring about water-soluble NO$_3^-$ ion and reduce the saturated vapor pressure of the surface water film to promote further adsorption of water molecules[25]. The precursor HNO$_3$ of NO$_3$ was formed during the photochemical reaction of the NOx hydrocarbon system during the study of winter aerosol pollution condition in the Kanto Plain, Japan[26]. The simultaneous increase in NO$_2$ concentration measured throughout the contamination process is considered as a substitute for O$_3$ in photochemical reactions. Studies have shown that the temperature and formation of NO$_3^-$ and SO$_4^{2-}$ in atmospheric particulates also have a great relationship. The increase of RH in the atmosphere and the increase of NH$_4^+$ concentration can speed up the conversion rate of NOx when studying the water-soluble ions in PM10 during atmospheric heavy pollution[16]. Some gases in the atmosphere (such as O$_3$, NO$_2$, H$_2$O$_3$, and NH$_3$) promote the heterogeneous reaction process of SO$_2$ on the exterior of dust[19, 27, 28]. Some researches suggested that the direct oxidation of SO$_2$ by NO$_2$ may exert an enormous function on the sulfate generation process[29-31]. The research on the heterogeneous reaction of SO$_2$ in the presence of NO$_2$ found that the two gas have synergistic effects on many oxides[27,32-36]. Adding Al$_2$O$_3$ particles and increasing NOx concentration can further raise the output of sulfate[32].

As the main basic gas component in the atmosphere, NH$_3$ has a great effect on the generation of secondary inorganic particles. Many scholars in the study of gaseous pollutants have focused on SO$_2$ and NOx, but not enough attention has been paid to NH$_3$. Effect of Reducing in PM2.5 concentration caused by SO$_2$ and NOx emission controlling will be offset by the rise in NH$_3$ emissions, which is unfavorable to the improvement of air quality[37]. Controlling NH$_3$ would be the most economical and effective way to reduce the concentration of fine particles when SO$_2$ and NOx have been controlled to a certain extent according to the experience of European and American countries[38]. Therefore, paying attention to the NH$_3$ emission problem and exploring the effect of ammonia on the secondary inorganic particulates in the atmosphere is of great significance in helping humans control particulate matter.

At present, most investigations on the heterogeneous reaction of gaseous pollutant on the surface of particulate matter focus on single component particulate matter, and there are few explorations of the reaction mechanism on
the surface of mixed particulate matter. Therefore, this experiment selects various types of metal oxide particles, and the mixture containing a plurality of metal oxides-coal ash as the reactant. The difference of heterogeneous reaction performance of diverse particles and the yield of secondary particulate matter with the change of external reaction environment and the heterogeneous reaction on various coal ash were explored. Also, the distinctions between coal ash and single type of particulate matter were compared. The metal oxides selected in this experiment include SiO₂, Al₂O₃, CaO, Fe₂O₃, and MgO. WH (White Heaven, Australia), MHU (Indonesia), and Centennial coal (Australia) were selected for the exploration of coal ash. This experiment explored the heterogeneous reaction of mixed gas (e.g. SO₂, NO₂, NH₃, and air) on the surface of the particles under ambient temperature and pressure based on the laboratory-built aerosol generating reactor. The secondary particles generated by heterogeneous reaction were investigated by ion chromatography.

2. Experimental sections

2.1 Sample preparation

The samples used in the experiment were five kinds of metal oxides: SiO₂ (Samchun Co., Ltd, Korea), Al₂O₃ (Duksan Co., Ltd, Korea), CaO (Duksan Co., Ltd, Korea), Fe₂O₃ (Daejung Co., Ltd, Korea) and MgO (Duksan Co., Ltd, Korea), and three kinds of coal ash made of WH (Australia), MHU (Indonesia), and Centennial (Australia). SiO₂, Al₂O₃, Fe₂O₃ and MgO particles used in the experiment were washed with ultrapure water and filtered. After repeating 3 times, the sample was dried in the oven for 24 h. The dried sample particles were sieved to separate particles with a particle size of less than 75 μm. The three coals were sieved, and coal sample with a particle size less than 75 μm were placed in a muffle furnace, and fully burned at 815 °C for 12 h to get coal ash sample for the experiment. All samples were purchased. The gases used in the experiment were listed as follows: SO₂ (Deokyang Co., Ltd, Korea), NO₂ (Deokyang Co., Ltd, Korea), NH₃ (Deokyang Co., Ltd, Korea), N₂ (Deokyang Co., Ltd, Korea) and air (79 % O₂ and 21 % N₂, Han-il s.g. Co., Ltd, Korea). The experiment used the mass flow meter (MFC) (MFC Korea Co., Ltd, Korea) to control the gases flow rate.

2.2 Experiment apparatus and procedure

Fig. 1 shows a schematic of the reaction system. The sample was first placed in the reactor which is a spherical object made of a three-necked flask and the whole reaction system was flushed with N₂ or air for 30 min, to remove the impurity gases in the reactor, in order to avoid impurities effect on the experimental results. Thereafter, the introduced gases, such as SO₂, NO₂, and NH₃, were uniformly mixed in mixing bottle, and then entered the reactor, and started the reaction with UV irradiation at room temperature. The end of the reactor was connected to a NaOH solution bottle, to neutralize unreacted acid gas. The temperature and humidity were recorded during the experiment process through a temperature and humidity meter connected to the reactor. After reaction, clean gas was continuously flushed through the reactor. Finally, sample particles were collected.
for detection and analysis. The mass of the sample used in each experiment was 0.5g and the total gas flow rate was 400ccm/min. Ion chromatography (IC, 882 Compact IC Plus) was used to detect the content of sulfate and nitrate. Surface properties of the particles were detected by the Brunner–Emmet–Teller method (BET, BELSORP-mini). Scanning electron microscope (SEM, JSM-6700F) was used to detect the morphological changes of the particles. Energy dispersive X-Ray spectroscopy (EDX–7421) was used to do the elemental analysis. Particle size analysis (PSA, Malvern Master Size MU2000) was used to detect the changes in particle size.

![Diagram](image)

Fig. 1. Schematic of the reaction system.

3. Results and discussion

3.1 Effect of metal oxide on the generation of secondary ultrafine particles

The reaction abilities of various oxide particles are distinct. The same quality of SiO₂, Al₂O₃, CaO, Fe₂O₃, and MgO were tested under UV light irradiation. The yield of sulfate and nitrate produced on each particle was different after 2 h reaction as shown in Fig. 2. The amounts of sulfate and nitrate formed on the surface of SiO₂ and Fe₂O₃ were relatively close and much lower than those of Al₂O₃, MgO, and CaO. Comparison of the salt yields formed on the particles showed that the order of the heterogeneous reactivity of the same mass oxide is: Al₂O₃>MgO>CaO>SiO₂, Fe₂O₃. This may be related to the fact that SO₂ and NO₂ participating in the reaction are both acid gases, so the hydroxyl-rich Al₂O₃ and the basic MgO and CaO have strong absorption and catalytic oxidation ability. The reactivity of Al₂O₃ is the most obvious among these oxides because each Al₂O₃ molecule can adsorb three hydroxy groups at the same time, while the surface of MgO may not have as many hydroxyated substances as alumina. MgO is more metallic than CaO, and more easily reacts with acid gases, so the reactivity of MgO is slightly higher than CaO. Near-neutral SiO₂ and Fe₂O₃ with poor surface properties show weaker reaction properties, which may be due to the fact that the adsorbed water on the surface of the two particles may to some extent inhibit the heterogeneous transformation of SO₂ and NO₂.

BET detection of the three kinds of particles with a higher reactivity was performed, and Table 1 shows the results. The specific surface area of Al₂O₃ is much larger than that of MgO and CaO, which may be one of the reasons for its high reactivity. At the same time, the effective reaction area of these three kinds of particles was calculated. In order to obtain a more accurate effective reaction area, the sample was taken out from the reactor after reaction, dissolved with ultra-pure water, filtered, and analyzed by ion chromatography to obtain the nitrate and sulfate amounts formed on the particles. Further, the amounts of metal nitrate and metal sulfate produced by the reaction were calculated, thereby calculating the amount of mineral oxide participating in this reaction, and multiplying by the BET specific
surface area of mineral oxide, to obtain the desired effective reaction area. This is called the corrected area, which is very close to the real reaction area. The calculation results listed in Table 1 show that the effective reaction area of Al₂O₃ is the largest among the three particles with the same quantity. It can be speculated that based on the above results, Al₂O₃ may contribute more to the heterogeneous reaction of atmospheric particles.

In order to investigate whether the morphology of the particles changed before and after reaction, SEM, EDX and PSA tests were carried out on Al₂O₃ particles which have the highest reactivity. SEM was used to compare the surface morphology of Al₂O₃ particles before (Fig. 3a) and after (Fig. 3b) reaction. The image shows that there are many large size particles before reaction, while there are many small size particles shown in the image after reaction. It can be concluded that the number of small size particles increases, while the number of large size particles decreases after the reaction. The EDX result shows that the sample contained no sulfur element before reaction (Fig. 4a) and the sulfur species was detected after reaction (Fig. 4b), which indicates that the particles formed a sulfur-containing substance after reacting with SO₂ and NO₂. The presence of sulfur-containing substances corresponds to the appearance of small particles in the SEM photograph. The results confirmed that the heterogeneous reaction of SO₂ and NO₂ on the exterior of the particles produces small particles-secondary particles.

By detecting and analyzing the particle size before and after reaction, it obtained results that were in accordance with the SEM test. Fig. 5 shows the specific particle size distribution. Before reaction, particles with a size of less than 2.5 μm accounted for 5.8 % of the total particles. After reaction, the proportion of particles with a size of less than 2.5 μm in all particles rose to 12.6 %. According to the

Table 1. Specific surface area and effective reaction area of Al₂O₃, MgO, and CaO

<table>
<thead>
<tr>
<th></th>
<th>aₑ (m²/g)</th>
<th>C₅O₄²⁻ (ppm)</th>
<th>C₅O₃⁻ (ppm)</th>
<th>M</th>
<th>αₛ (0.001D) (m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>113.93</td>
<td>335.52</td>
<td>42.96</td>
<td>101.96</td>
<td>371.86</td>
</tr>
<tr>
<td>MgO</td>
<td>5.83</td>
<td>150.18</td>
<td>45.08</td>
<td>40.30</td>
<td>11.32</td>
</tr>
<tr>
<td>CaO</td>
<td>1.57</td>
<td>63.56</td>
<td>8.99</td>
<td>56</td>
<td>1.62</td>
</tr>
</tbody>
</table>

Note: as, BET BET specific surface area; C₅O₄²⁻ sulfate concentration; C₅O₃⁻ nitrate concentration; M relative molecular mass; αₛ effective reaction area.
analysis result, particles with a size of less than 2.5 μm were significantly increased after reaction. It is concluded that the heterogeneous reaction in the atmosphere makes an important contribution to fine particles from this phenomenon.

Fig. 3. SEM photographs of Al₂O₃ particles: (a) before reaction; (b) after exposure to SO₂ and NO₂ for 2 h.

Fig. 4. EDX analysis of Al₂O₃ particles: (a) before reaction; (b) after exposure to SO₂ and NO₂.

Fig. 5. Particle size distribution on the surface of Al₂O₃: (a) before reaction; (b) after exposure to SO₂ and NO₂ for 2 h.

3.2 Effect of reactant mass on the heterogeneous reaction of metal oxide

The mass of reactants (i.e. the concentration of reactants in the reactor) is also a factor influencing the heterogeneous reaction of the particulate matter. Two mass conditions of 0.5 and 1.0 g were selected to investigate the
heterogeneous reaction on Al₂O₃ particles under different reactant concentrations. After 2 h reaction, IC results as shown in Fig. 6 show that the more particles that were involved in the reaction, the less sulfate and nitrate were formed on per unit mass reactant when the other reaction conditions were consistent. When the mass of the reactant was 1.0 g, the total yield of sulfate and nitrate after the reaction was significantly higher than the yield when the mass of the reactant was 0.5 g. The growth rate of the product did not increase by a multiple of the mass ratio. This may be related to the contact area per unit mass reactant with the reaction gas. In the same reactor, the more particles that were involved in the reaction, the smaller the contact area per unit particles with reaction gas. The reduction of the effective reactive sites of particles during the reaction results in a decrease in the reactivity and a decrease in the gas conversion rate and leads to a decrease in the amount of product. This indicates that the reactant concentration has a large effect on the heterogeneous reaction.

Fig. 6. Concentrations of (a) NO⁻ and (b) SO₄²⁻ generated on Al₂O₃ under the reactant mass condition of (0.5/1.0) g after exposure to SO₂ and NO₂ for 2 h with ultraviolet light irradiation.

3.3 Effect of NO₂ on the heterogeneous reaction of particulate matter

NO₂ and SO₂ have a synergistic function on the surface of particles and NO₂ can speed up the oxidation of SO₂ on particles to produce more sulfate. O₂ has a great effect on the reaction atmosphere during the process of NO₂ promoting the oxidation of SO₂ to sulfate. N₂ and air were selected as carrier gases in the experiment respectively, and the heterogeneous reaction on Al₂O₃ under two conditions of SO₂ and SO₂/NO₂ gas coexisting was studied.

It was found that NO₂ could not exhibit a synergistic effect on SO₂ when N₂ was used as a carrier gas through comparative experimental research as shown in Fig. 7 which might be due to the fact that the photolysis of NO₂ requires the participation of oxygen and the formed oxidizing substances promotes the oxidation of SO₂ on particles. No synergy between SO₂ and NO₂ when no oxygen exit and the two gas are competitive in the reaction environment. The introduced NO₂ will compete with SO₂ on particles for the active site to inhibit the
conversion of SO₂. When air is selected as the carrier gas, NO₂ significantly promotes the heterogeneous reaction of SO₂ on Al₂O₃ as shown in Fig. 8.

The experimental results with the presence and the absence of NO₂ were compared when air was taken as the carrier gas to participate in the reaction and studied the reaction of SO₂ on Al₂O₃ particles. The effect of NO₂ on the reaction progress was explored by comparing the amount of sulfate produced after the reaction. It was found that the sulfate output increases significantly when NO₂ participates in the reaction, which fully reflects the synergistic effect of NO₂ on SO₂. This may be because NO₂ on the particles will form a water-soluble nitrate during the heterogeneous absorption process when there is surface adsorbed water on the particles. Photolysis of adsorbed nitrates can bring about oxidizing actives, such as OH radicals and reactive oxygen species, which can cause SO₂ to oxidize on the particles, thereby accelerating the formation of sulfate. And the formed surface nitrate material can enhance hygroscopicity of the mineral oxide and the surface water content. This allows the oxidation process of SO₂ to occur in the liquid phase and increases the conversion efficiency of SO₂ to sulfate. Laboratory research found that NO₂ could promote the oxidation of SO₂ and generate more sulfate, which also indicates that the complex pollution process would affect the atmospheric migration and transformation process of SO₂ and NO₂.

Fig. 7. Concentrations of (a) NO₃⁻ and (b) SO₄²⁻ generated on Al₂O₃ with ultraviolet light irradiation, when N₂ was used as carrier gas in the presence/absence of NO₂.

Fig. 8. Concentrations of (a) NO₃⁻ and (b) SO₄²⁻ generated on Al₂O₃ with ultraviolet light irradiation, when air was used as carrier gas in the presence/absence of NO₂.
The experimental results with the presence and the absence of NO₂ were compared when air was taken as the carrier gas to participate in the reaction and studied the reaction of SO₂ on \( \text{Al}_2\text{O}_3 \) particles. The effect of NO₂ on the reaction progress was explored by comparing the amount of sulfate produced after the reaction. It was found that the sulfate output increases significantly when NO₂ participates in the reaction, which fully reflects the synergistic effect of NO₂ on SO₂. This may be because NO₂ on the particles will form a water-soluble nitrate during the heterogeneous absorption process when there is surface adsorbed water on the particles. Photolysis of adsorbed nitrates can bring about oxidizing actives, such as OH radicals and reactive oxygen species, which can cause SO₂ to oxidize on the particles, thereby accelerating the formation of sulfate. And the formed surface nitrate material can enhance hygroscopicity of the mineral oxide and the surface water content. This allows the oxidation process of SO₂ to occur in the liquid phase and increases the conversion efficiency of SO₂ to sulfate. Laboratory research found that NO₂ could promote the oxidation of SO₂ and generate more sulfate, which also indicates that the complex pollution process would affect the atmospheric migration and transformation process of SO₂ and NO₂.

3.4 Effect of humidity on the reaction

Humidity is interrelated to the heterogeneous reaction of SO₂ and NO₂ on metal oxides. High RH can promote the production of sulfate on the surface of the particles. This experiment used two sets of humidity conditions to compare the influence of humidity on the heterogeneous reaction. Air was used to flush the reactor for 30 min before the reaction. On the one hand, the impurity gas in the reactor could be removed. On the other hand, the air passing through the water bottle could also provide a certain humidity environment for the reaction particles. After starting the reaction, one set of experiments used dry gas as the low humidity condition experimental group and the other set used the air by passing through distilled water (controlling the temperature of distilled water), to provide a relatively high humidity environment for the whole reaction process as the high humidity experimental group. By comparing the yields of sulfate and nitrate produced by the two groups as shown in Fig. 9, it was found that the yield of sulfate produced by alumina and mixed gas under relatively high humidity condition was higher, while the yield of nitrate was lower. This indicates that surface-adsorbed water affects the generation of sulfate secondary aerosol.

According to previous studies, it is known that the reaction of SO₂ with mineral dust can be carried out by two processes: reaction with surface active sites or reaction with surface-adsorbed water. The adsorbed water can take up the surface active site, thereby reducing the surface’s reactivity to SO₂, but it can also accelerate the hydration of SO₃[^6].[^30] The experimental results show that the promotion effect of the water molecules’ hydration of SO₂ under high humidity conditions is much higher than the inhibition effect of SO₂ adsorption and conversion caused by the surface active sites of adsorbed water. During the reaction, water vapor can be directly combined with SO₂ to form H₂SO₃ in the reactor. SO₃²⁻ is
formed on particles and then oxidized to $\text{SO}_4^{2-}$. Alternatively, water vapor can be adsorbed on the surface of the particles at low RH. Then, $\text{SO}_2$ is oxidized to $\text{SO}_4^{2-}$ or $\text{HSO}_3^-$ by a heterogeneous reaction, and is finally oxidized to form $\text{SO}_4^{2-}$ or $\text{HSO}_4^+$. It is known that based on previous studies, Lewis acid sites, hydroxyl and oxygen vacancies play a significant role in the surface chemistry of $\text{SO}_2$[40]. The interaction of $\text{O}_2$ and $\text{H}_2\text{O}$ with the surface of the metal oxide particles can produce reactive oxygen and hydroxyl groups. Therefore, the water adsorbed on the particles can speed up the conversion of $\text{SO}_2$ on the surface of the particles to produce more sulfate[41]. Moreover, the higher RH helps the water vapor to form a water film on the surface of the particles and the water film can diffuse the sulfate formed on the surface of particles to promote the renewal of sample surface, which is favorable for the contact of $\text{SO}_2$ with more reactive sites and promotes the reaction proceeding in the forward direction. Thus, more sulfate is formed under high humidity conditions.

This experiment shows that the increase of RH is not conducive to the conversion of NOx, and NO$^{3-}$ decreases with the increase of RH, which may have a great relationship with the amount of adsorbed water. At the beginning of the reaction, the number of water molecules adsorbed on the surface of the particles may be roughly equivalent under high RH and low RH, and the surface adsorbed water is rapidly involved in the heterogeneous reaction so that NO$_2$ is converted into nitrate. However, as the reaction progresses, the water provided by this experiment is less and less under low RH in the reactor, while the water content of high RH is always at a high level. In the initial stage of the reaction, the reaction rate of the particles under high RH conditions should be higher than that under low RH. Thus, more sulfate is produced at high RH than lower RH conditions.

A large amount of tetravalent sulfide produced may occupy more active sites for NO$_2$ conversion on the surface of the particles, thereby inhibiting the conversion of NO$_2$ gas to nitrate. Therefore, more and more sulfates are formed under high RH conditions, and the sites for supplying NO$_2$ are less and less, resulting in a decrease in the amount of nitrate produced under high RH conditions. At the same time, it is also possible that during the reaction, NO$_2$ and water molecules have a competitive adsorption relationship on the particles’ surface[42]. When
the RH increases, the adsorbed water will also increase. The excess adsorbed water on the surface of the particles covers the reactive sites, which inhibits the further adsorption and conversion of NO₂. This hinders the progress of the heterogeneous reaction. Experimental results show that the competitive effect between NO₂ and the adsorbed water and the occupation function of the surface-active sites by the newly formed sulfate particles are stronger than the conversion of the combination of NO₂ and water molecules in the reaction environment provided by the laboratory.

3.5 Effect of NH₃ on heterogeneous reactions

NH₃ has a non-negligible effect on the heterogeneous reaction of SO₂ and NO₂ on metal oxide particles. In order to study the effect of NH₃ on the reaction process, the heterogeneous reaction on Al₂O₃ in the presence and absence of NH₃ were compared. Analysis results (refer Fig. 10) show that NH₃ has a significant effect on the heterogeneous reaction after 8 h of reaction under UV light irradiation. The yield of nitrate is much higher than that without NH₃ after reaction when NH₃ is present. The change in the yield of sulfate is not obvious, only a slight increase. This may be because NH₃ is an alkaline gas and both SO₂ and NO₂ are acid gases. When NO₂, SO₂, and NH₃ coexist, the acid-base interaction among three gases and the redox process between NO₂ and SO₂ can take place. The redox of NO₂ and SO₂ can accelerate the formation of sulfate. The adsorbed NO₂ timer intermediate N₂O₄ can oxidize and adsorb SO₂ to form sulfate species, while N₂O₄ is reduced to produce nitrite species. Moreover, the coexistence of two acid gases and ammonia gas will produce a composite effect. SO₂ and NO₂ will promote the conversion of NH₃ from the coordinated NH₃ of the Lewis acid site to the adsorption of NH₄⁺ by the Brønsted acid site. When NH₃ is present, it promotes the increase of hygroscopicity of the surface of the particles.

![Fig. 10. Concentrations of (a) NO₃⁻ and (b) SO₄²⁻ generated on Al₂O₃ in the presence/absence of NH₃ after exposure to SO₂ and NO₂ for 8 h with ultraviolet light irradiation.](image)

More H₂O and O₂ interact with particles to produce more active oxygen and hydroxyl groups, thereby increasing the surface reactive sites. At the same time, the introduction of NH₃ also changes the pH value of the reaction environment. NH₃ can neutralize the acidic substances, such as H₂SO₄ and HNO₃, formed during the reaction, and promote the reaction in the positive reaction direction, which reduces
the acidity of the whole reaction system, further promoting the conversion of acid gas on the surface of alkaline particles, and producing more secondary particles. The sulfate yield did not change significantly, because the solubility of SO$_2$ decreased significantly, as the acidity of the particles increased$^{2, 44}$. On the acidic NH$_4$(SO$_4$)$_2$ particles, the heterogeneous reaction between SO$_2$ and NO$_2$ was inhibited. Therefore, the yield of sulfate did not change significantly.

In addition, the difference in the formation of secondary particles on the Al$_2$O$_3$ particles under the conditions of the ammonia flow rate of 50 and 100 ccm/min was compared. It was found that the nitrate production decreased significantly, and the sulfate production was almost unchanged when the ammonia concentration decreased after 8 h of reaction as shown in Fig. 11. The presence of ammonia mainly affects the production of nitrate, and the effect on sulfate is weak, which is in keeping with the results of previous research$^{45}$. This may be related to the acid–base effect between NO$_2$ and NH$_3$, or between SO$_2$ and NH$_3$. When the ammonia concentration ratio is high, the amount of sulfate and nitrate produced increases proportionally. This shows that the higher the relative proportion of ammonia, the higher the conversion rate of SO$_2$ and NO$_2$.

3.6 Effect of the ratio of SO$_2$ to NO$_2$ on the formation of secondary particles in the presence of ammonia

The concentration ratio of SO$_2$ to NO$_2$ also affects the formation of secondary particles. Three concentration ratio conditions were selected during the experiment. The SO$_2$ and NO$_2$ concentration ratios were 1:2, 2:2, and 2:1, respectively. It was found from the IC result as shown in Fig. 12 that the sulfate production increased positively, and the nitrate production decreased negatively with the increase of SO$_2$ concentration when the ammonia concentration was constant. With the increase of NO$_2$ concentration, the sulfate production decreased negatively, and the nitrate production increased positively.
heterogeneous reaction by using oxide as a reactant to explore the difference in reaction performance under different conditions. The actual reaction in the atmosphere is that many different types of particles are mixed together to form a mixed system and various reactions occur. To investigate the difference in the heterogeneous reaction between a mixture and a single type oxide, the heterogeneous reaction of coal ash and single component oxide were compared. The types of coal and the composition of coal vary, so the coal ash composition is also different. The composition of coal ash is complex, but the main components are consistent with the main components of atmospheric particulate matter. In order to explore the difference in the heterogeneous reaction of different components of coal ash, the ash obtained by burning three kinds of coal raw materials were selected as reactants.

The elemental analysis results as shown in Table 2 of three kinds of coal ash shows that the content of SiO₂ in Centennial is the highest, the content of Al₂O₃ in WH is the highest, and the content of Fe₂O₃ in MHU is the highest. The contents of the Al₂O₃ components in these three raw materials are quite different. IC result as shown in Fig. 13 displayed that the WH coal ash with high Al₂O₃ content in raw coal has the most sulfate and nitrate formed after the reaction.

The secondary particulate matter produced on the surface of MHU with high Fe₂O₃ content is inferior to WH. The sulfate and nitrate amounts produced on the Centennial coal ash, which is rich in SiO₂, are much lower than the first two coal ashes. It is speculated that the results of this experiment should be related to the property of the main components of the coal ash.

3.7 Heterogeneous reaction on coal ash surface

Most researchers have studied the

![Fig. 12. Concentrations of (a) NO₃⁻ and (b) SO₄²⁻ generated on Al₂O₃ under SO₂:NO₂ ratio condition of 50/100, 100/100, and 100/50, after exposure to SO₂ and NO₂ for 8 h with ultraviolet light irradiation.](image)
The results of the three coal ash reactivities after experiments were consistent with the order of the Al\(_2\)O\(_3\) content amount in coal ash. According to previous experimental results, Al\(_2\)O\(_3\) is the most reactive oxides in several metal oxides, so Al\(_2\)O\(_3\) may make a relatively significant influence in the heterogeneous reaction of the mixture.

At the same time, it was found that the Al\(_2\)O\(_3\) content in the WH ash is lower than that of the single component Al\(_2\)O\(_3\) sample in same reaction quality. Theoretically, according to the previously obtained sequence of different oxides, the secondary particles formed on the surface of the mixture WH particles should be relatively less compared to the same mass of Al\(_2\)O\(_3\) as the reactant. However, the experimental results show that the yields of sulfate and nitrate formed on the mixture WH ash are higher than that of Al\(_2\)O\(_3\) with the same reactant mass. On the one hand, this may be related to the physical properties of the two samples. Although the Al\(_2\)O\(_3\) particles used in the experiment and the coal ash used are both less than 75 \(\mu\)m, the composition of the coal ash particles is relatively looser, which may increase the reaction area for the reaction, thereby providing more surface-active sites for the particles. The conversion of SO\(_2\) and NO\(_2\) on particles is promoted so that the secondary aerosol production is increased. On the other hand, it is also possible that because the coal ash is a mixture of various oxides, a synergistic reaction may occur between different types of oxide particles and promote the conversion of SO\(_2\) gas. This makes the reactivity of the mixture higher than the reactivity of a single component particle. The experimental results show that the components of the mixture have a synergistic effect on the heterogeneous reaction of SO\(_2\).

Table 2. XRF results of WH, MHU, and Centennial coal ash (unit: wt%)
there may be synergy among particles.

Table 3. Specific surface area and conversion amount of SO₂ on the per unit area of Al₂O₃, WH, MHU, and Centennial coal ash

<table>
<thead>
<tr>
<th></th>
<th>Centennial</th>
<th>MHU</th>
<th>WH</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>aₙₐ BET (m²/g)</td>
<td>27.68</td>
<td>38.16</td>
<td>5.39</td>
<td>113.93</td>
</tr>
<tr>
<td>C₈O₄²⁻ (ppm)</td>
<td>71.99</td>
<td>152.66</td>
<td>517.71</td>
<td>335.52</td>
</tr>
<tr>
<td>CNO₃⁻ (ppm)</td>
<td>106.46</td>
<td>97.91</td>
<td>122.96</td>
<td>42.96</td>
</tr>
<tr>
<td>(m-SO₂) g/m²</td>
<td>0.08669</td>
<td>0.13335</td>
<td>3.20273</td>
<td>0.09816</td>
</tr>
<tr>
<td>(m-NO₃) g/m²</td>
<td>0.14267</td>
<td>0.09518</td>
<td>0.84652</td>
<td>0.01399</td>
</tr>
</tbody>
</table>

Note: as, BET_BET specific surface area; C₈O₄²⁻_sulfate concentration; CNO₃⁻_nitrate concentration; (m-SO₂) g/m²_conversion amount of SO₂ on per unit area; (m-NO₃) g/m²_conversion amount of NO₃ on per unit area.

4. Conclusions

The heterogeneous reactivities of SO₂ and NO₂ on the surface of various types of metal oxides are distinct. Al₂O₃ particles show excellent reaction performance. The reactivity of CaO and MgO is inferior to that of Al₂O₃. SiO₂ and Fe₂O₃ show worse reaction performance. RH, the mass of particulate matter involved in the reaction, and the concentration of SO₂ and NO₂ exert a vital function on the yield of the product. NO₂ exhibit a significant synergistic effect on the conversion of SO₂ on Al₂O₃ in the presence of oxygen. When there is no oxygen in the environment, NO₂ shows no synergistic effect on the heterogeneous reaction of SO₂. NH₃ shows a crucial synergistic effect on the heterogeneous reaction of SO₂ and NO₂ on the surface of Al₂O₃. The yield of secondary nitrate is significantly increased with the growth of NH₃ concentration. By comparing the heterogeneous reaction on single metal oxide and coal ash, it is clearly identified that different metal oxides have a synergistic effect for secondary ultratine particle generation.

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