

The roles of heterogeneous chemical processes in the formation of an air pollution complex and gray haze

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Urban and regional air pollutions are characterized by high concentrations of secondary pollutants such as photo-oxidants (mainly ozone) and fine particulate matter, which are formed through chemical reactions of the primary pollutants emitted from various sources. The accumulation of these pollutants under stagnant meteorological conditions results in the formation of gray haze, reducing visibility and causing major impacts on human health and climate. In an air pollution complex, the co-existence of high concentrations of primary and secondary gaseous and particulate pollutants provides a large amount of reactants for heterogeneous reactions on the surface of fine particles; these reactions change the oxidizing capacity of the atmosphere, as well as chemical compositions along with the physicochemical and optical properties of particulate matter, thereby accelerating formation of the air pollution complex and gray haze. Using *in situ* technologies, such as diffuse reflectance infrared Fourier-transform spectroscopy and single-particle Raman spectroscopy, we systematically investigated the reaction kinetics and mechanisms of gaseous pollutants (i.e., NO₂, SO₂, O₃, and formaldehyde) on the surfaces of the major components of atmospheric particles such as CaCO₃, kaolinite, montmorillonite, NaCl, sea salt, Al₂O₃, and TiO₂. We found that the main reaction products were sulfate, nitrate, or formate, which can change the hygroscopicity and light extinction parameters of those particles significantly. By analyzing the reaction kinetics of these heterogeneous reactions, we identified synergetic mechanisms of the three ternary reaction systems, i.e., NO₂-particles-H₂O, SO₂-particles-O₃, and organics/SO₂-particles-UV illumination. These synergetic mechanisms can provide experimental and theoretical bases for understanding the feedback mechanisms and nonlinear processes in the formation of an air pollution complex and gray haze.

fine particles, secondary pollutants, oxidizing capacity, ternary reaction, nonlinear processes

1 Introduction

China's rapid economic development and urbanization has resulted in substantial emissions of pollutants into the atmosphere. The coexistence of numerous air pollutants with high concentrations and the complicated interactions among them leads to the formation of an air pollution complex and gray haze. The air pollution complex is characterized by an increase in the oxidizing capacity of the

atmosphere, reduced atmospheric visibility, and the deterioration of environmental quality throughout the entire region; in essence, the air pollution complex features the interactions between the sources and sinks of air pollutants, the coupling processes of the transformation of pollutants, and the synergetic environmental impacts of the air pollutants [1–4]. Field observations in Beijing and the Pearl River Delta have demonstrated the coexistence of fine particulate matter and gaseous pollutants, particularly oxidants, at high concentrations in both regions [3–9] exhibiting typical characteristics of an air pollution complex. This indicates that the air pollution complex in China's

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major economically developed regions has become an increasingly more serious environmental problem.

The key to studying the formation mechanism of the air pollution complex at a regional scale lies in the quantitative determination of the regional atmospheric oxidizing capacity and understanding the formation mechanism and kinetics of photochemical oxidants under high concentrations of fine particles [2]. To date, several field observations and model simulation studies have investigated the formation mechanism of the air pollution complex, but laboratory studies on the chemical reaction processes have been very limited; thus, to some extent, this has hindered fundamental theoretical research on the formation mechanism of the air pollution complex.

The three study tools of atmospheric chemistry (laboratory studies, field observations, numerical simulations) have demonstrated the importance of heterogeneous reactions, which play the central role in the transformation of troposphere gaseous pollutants and the formation of secondary aerosols [10–13]. Heterogeneous reactions can change the chemical compositions and surface features of particulate matter such as particle hygroscopicity, toxicity, and optical properties [14–19] and thus cause a significant impact on human health and ecological and climate systems. Through laboratory study, investigating the kinetics and mechanism of heterogeneous reactions at the molecular level can determine the main mechanisms and kinetic parameters in the formation mechanism of the air pollution complex [20], identify the synergetic effects under a variety of reaction conditions, and provide key parameters for numerical simulations to further illustrate the nonlinear characteristics of the air pollution complex and control strategy. Considering the importance of heterogeneous reactions in the formation of the air pollution complex and its impact on the environment and climate, to accurately simulate the atmospheric chemistry processes, provide air pollution control policy suggestions, and evaluate aerosol radiative forcing, one must have a thorough understanding of the atmospheric heterogeneous reactions.

Currently, research on heterogeneous chemistry on the surface of atmospheric particles is still in its preliminary stages compared to homogeneous gaseous reactions, particularly in understanding the role of particle surface structure in the reactions at the molecular level. In the ambient air, three-phase (gas–liquid–solid) reactions in the presence of water vapor may occur. In addition to chemical reactions, gas–liquid and gas–solid based liquid mass transfers and other physical processes may take place, leading to further complexity in studying heterogeneous reaction kinetics and mechanism. To overcome these difficulties, we established an integrated method for studying the heterogeneous reactions on particle surfaces in our laboratory. We then investigated a variety of atmospheric heterogeneous reaction processes and identified synergetic mechanisms of ternary reactions in the atmosphere. Using these ternary reactions,

we discussed the roles of heterogeneous reaction processes in the formation of the air pollution complex and gray haze.

2 Research methods

The atmospheric heterogeneous reaction study focused on the gas–solid–liquid reaction on the surface of micro- and nanoparticles. The composition and structure of bulk and the surface of solid particles determine the active sites participating in the reaction, and therefore affect the reaction process and rate. To study the influence of surface properties on the reaction, and to assure experimental reproducibility, one must characterize the surface physicochemical properties of the particles comprehensively. In addition, during heterogeneous reactions, the reaction system typically is not uniform and could be far from equilibrium [2]. Therefore, *in situ* and online monitoring of the reaction kinetics is required.

Our laboratory established an integrated method for studying the heterogeneous reactions on particle surfaces. This method includes monitoring the reaction process and characterizing the physicochemical properties of the particle surface. The instruments used and experimental purposes are listed in Figure 1. X-ray diffraction (XRD), scanning electron microscopy (SEM), laser particle size analysis (LPS), simultaneous derivative thermogravimetry analysis (SDT), and BET surface area analysis (SAA) were used to characterize the physicochemical properties of the particles, including the crystalline structure, morphology, size distribution, thermal properties, and BET surface area. To monitor the processes of heterogeneous reactions, a flow reaction system with diffuse reflectance infrared Fourier transformation spectroscopy (DRIFTS) and an individual particle flow reaction system with micro-Raman spectroscopy were used to continuously measure the reaction products *in situ*. A noninvasive method was developed for transferring the sample from the flow reaction system after the reaction to characterize the surface and bulk product, morphology, and hygroscopicity by XPS, SEM, and IC analyses to confirm the reaction products with the *in situ* methods. Finally, on the basis of the comprehensive analyses of the reaction process and the physicochemical properties of the particles, the mechanisms of the heterogeneous reactions and influence factors were analyzed.

Using the flow reaction system with DRIFTS (Figure 2) and optimized sample preparing method [21], we investigated the reaction kinetics and measured kinetic parameters of the heterogeneous reactions. The reaction products were analyzed qualitatively and quantitatively, and the reaction mechanisms were concluded and confirmed, as described previously [22–24]. To study the heterogeneous reactions and multiphase reactions involving gas–liquid–solid phases in the presence of liquid water, we established the flow reaction system with a micro-Raman spectrometer (Figure 3)

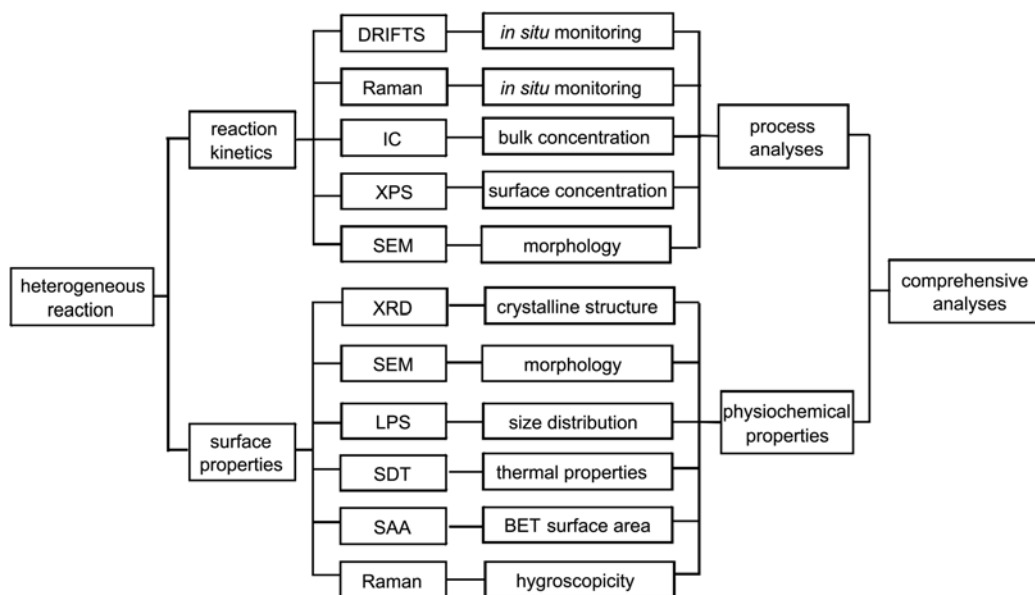


Figure 1 Comprehensive methods for studying heterogeneous reactions.

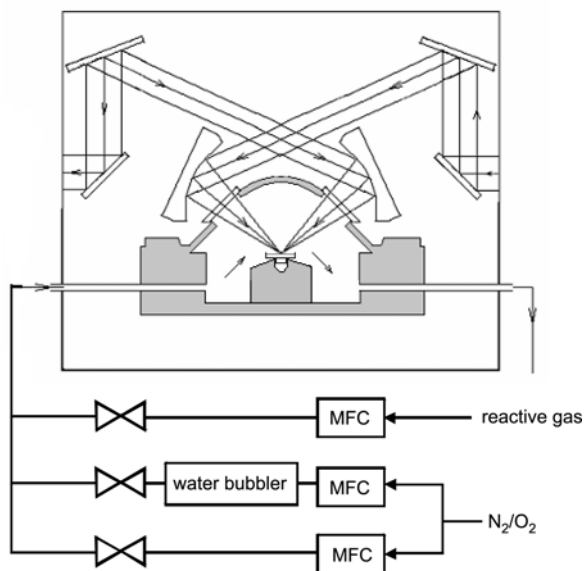


Figure 2 *In situ* DRIFTS reaction system.

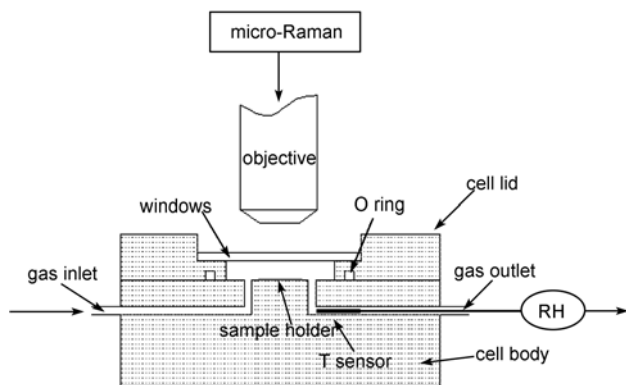


Figure 3 Schematic diagrams of the micro-Raman spectrometer with the reaction system for multiphase reactions.

to study the multiphase reactions on individual particles [25] and for the hygroscopicity study of particles [26].

3 Major reaction processes

The heterogeneous reactions of NO_2 , SO_2 , O_3 , and HCHO with various major particle components including CaCO_3 , Al_2O_3 , TiO_2 , kaolinite, montmorillonite, NaCl , and sea salt were investigated using the integrated experimental method developed in our laboratory. Kinetic parameters such as the reaction order and uptake coefficient were measured, the reaction mechanisms were investigated, and a kinetics model of heterogeneous reactions was developed. Based on these results, the synergetic effects in the ternary heterogeneous reactions were also examined.

3.1 NO_2 -particles- H_2O reaction

Heterogeneous reactions of NO_2 with mineral particles including CaCO_3 , kaolinite, and montmorillonite were investigated in our laboratory using the *in situ* DRIFTS reaction system combining IC, XPS, and SEM under dry and humid conditions. We found the reaction was slow and might have had a negligible influence on the atmospheric chemistry, whereas in the presence of water, the reaction of NO_2 on the surface of weakly hygroscopic mineral particles was accelerated significantly. The product, nitrate, led to the enhancement of the hygroscopicity of the particles, demonstrating a ternary synergetic effect in the NO_2 -particles- H_2O reaction system.

Our data indicated that humidity could not only affect kinetic parameters such as the reactive uptake coefficient and reaction order of the reaction of NO_2 on the surface of

mineral particles, but the reaction mechanism as well. Under dry conditions, oxygen vacancy dissociates surface water and forms the stable surface $-OH$, which has a determined effect on the reaction. Before the surface $-OH$ is depleted, the reaction order is 2; after that, the bulk $CaCO_3$ participates in the reaction and forms more surface $-OH$, and the reaction order is zero. The following reaction process was concluded from the experimental results: with the increase in relative humidity (RH), water condenses gradually on the surface of the particle. At high RH ($>52\%$ in this study), NO_2 reacts with water in a disproportionate way, forming nitric acid and HONO, and the reaction order is 1. The reaction product, nitrate, enhances the hygroscopicity of the $CaCO_3$ particle, resulting in a change in particle morphology under certain RH. Even at low RH ($<20\%$), the reaction of NO_2 with $CaCO_3$ is not limited to the particle surface; instead, it can proceed irreversibly until the entire $CaCO_3$ particle is converted to form $Ca(NO_3)_2$ droplets. Laskin *et al.* also observed this phenomenon in the reaction of HNO_3 with $CaCO_3$ [27]. In the atmosphere, $CaCO_3$ undergoing this process can transform into $Ca(NO_3)_2$ partly or completely, which can change the shape and size of the particles and further alter the light scattering and absorption of the particles. In addition, internal mixing of $CaCO_3$ - $Ca(NO_3)_2$ particles can increase the effective number of cloud condensation nuclei in the atmosphere.

The photolysis of HONO is an important source of the atmospheric OH radical, whose source remains unclear. One study reported that the reaction of NO_2 on soot particles can produce HONO [28]. Our study showed that the heterogeneous reaction of NO_2 on $CaCO_3$ particles can produce NO_2^- [29] (Figure 4). The reaction of NO_2 on the surface of $CaCO_3$ particles forms $Ca(NO_3)_2$, which reduces the pH value of the particle; thus, under acidic conditions, NO_2^- can evaporate into the gas phase in the form of HONO, which could be an important source of HONO in the atmosphere. This speculation needs to be confirmed by detecting HONO in the gas phase.

Kaolinite and montmorillonite are representative 1:1 and 2:1 type phyllosilicates. The study of their heterogeneous reactions is important for understanding the heterogeneous reactions of clay mineral particles. Our study on the heterogeneous reactions of NO_2 on kaolinite and montmorillonite particles revealed that (1) NO_2 is disproportionated on kaolinite particles, forming nitric acid and nitrous acid; (2) RH has an important effect on the heterogeneous reaction on kaolinite particles (under dry conditions, the reaction order is 2 and under humid conditions it is 1); (3) an increase in RH can reduce the uptake rate of NO_2 on kaolinite particles, but can increase the capability for the reaction to continue; the reaction of NO_2 on montmorillonite is first order and NO_2 disproportionates on the particles, forming nitric acid and HONO after adsorbing on the particles; (4) the reactive uptake coefficient is independent of the NO_2 concentration,

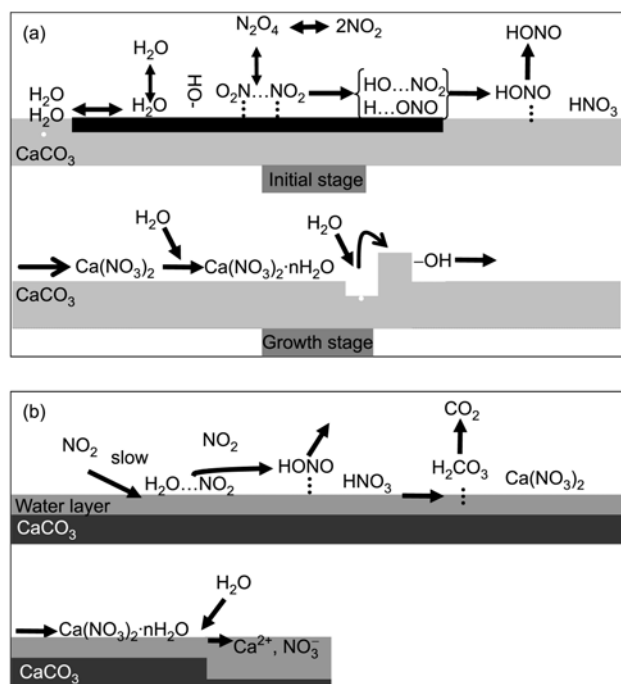


Figure 4 Schematic diagrams of the mechanism of NO_2 reaction on the surface of $CaCO_3$ particles under dry (a) and wet (b) conditions (reproduced with permission of the authors of ref. [29]).

but is associated with RH. Under dry conditions, the reactive uptake coefficient for NO_2 on Na-montmorillonite and Ca-montmorillonite was $(1.14 \pm 0.28) \times 10^{-8}$ and $(7.49 \pm 2.28) \times 10^{-7}$, respectively; under dry conditions, the heterogeneous reaction on Na-montmorillonite only occurs on the particle surface instead of between layers, whereas the reaction on Ca-montmorillonite can occur between layers due to the strong coordinating ability of Ca^{2+} and NO_3^- ; the increase in RH can reduce the heterogeneous reaction rate while enhancing the capability of the reaction of NO_2 on montmorillonite to continue [30].

To understand the heterogeneous reaction of NO_2 with sea salt particles in the coastal city air, we studied the heterogeneous reaction of NO_2 with sea salt particles at 0% and 20% RH. The reaction order of nitrate formation with respect to NO_2 was 2. At 0% and 20% RH, the reactive uptake coefficient in the growth period was $(5.51 \pm 0.19) \times 10^{-7}$ and 1.26×10^{-6} , respectively. Below 30% RH, $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ on the surface of sea salt form liquid water spots on the particle surface by releasing combined water and adsorbed water, which enhance the capability for the reaction to continue. Therefore, using only the data obtained from the study on the heterogeneous reactions of NaCl can underestimate the reactivity of the heterogeneous reactions of sea salt [31].

The above results demonstrate that the presence of water can not only affect the reactive uptake coefficient of NO_2 on particles, but it can also alter the reaction mechanism and

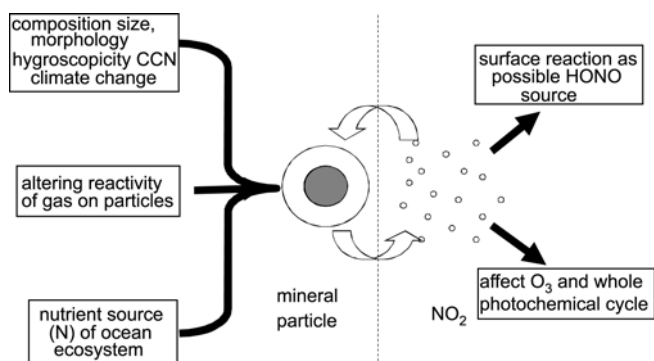


Figure 5 The heterogeneous reaction of NO_2 on mineral particles and its impacts on the environment and climate.

reaction products. Furthermore, the reaction product can change the optical properties, hygroscopicity, and CCN activity, which can further change the air visibility and the effect of aerosol on climate [32]. Moreover, HONO produced in the reaction can be photolyzed, forming an OH radical, which can influence the atmosphere oxidation capability. In addition, nitrate formed in the reaction can be a source of nutrients and thus affect the terrestrial and marine ecosystems. The heterogeneous reaction of NO_2 on particles and its impact on the environment and climate are depicted in Figure 5.

3.2 The SO_2 -particles- O_3 reaction

The gas phase oxidation of SO_2 and ozone (O_3) could produce SO_3 . This is a slow reaction in the atmosphere and it has a negligible contribution to the formation of sulfate in the troposphere. However, our experiments showed SO_2 adsorbed on the particle surface, forming sulfite, which can be rapidly oxidized to sulfate by O_3 [33, 34].

SO_2 oxidation by O_3 on the surface of CaCO_3 particles proceeds via two stages, as depicted in Figure 6: SO_2 adsorbs on the surface of CaCO_3 particles and forms sulfite; sulfite is oxidized into sulfate by O_3 [33, 34]. The reaction is first order for SO_2 and zero order for O_3 . Under the experimental conditions, the oxidation of SO_2 and O_3 in gas phase was negligible, and the adsorption of SO_2 was the

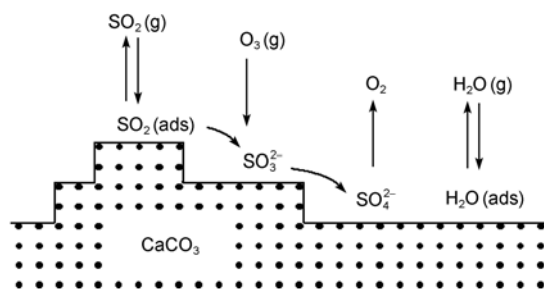


Figure 6 Schematic diagram of the mechanism of SO_2 oxidation by O_3 on a CaCO_3 surface reproduced with permission of the authors of ref. [34].

rate-determining step. When the RH was 40%, the steady-state uptake coefficient of SO_2 was independent of the concentrations of SO_2 and O_3 . However, the steady-state uptake coefficient of SO_2 increased with the increase in RH. The amount of water adsorbed on the surface of CaCO_3 particles increased as the reaction proceeded, indicating the increasing hygroscopicity of the particles and the acceleration of the oxidation rate caused by water. This suggests the importance of adsorbed water to the reaction.

The oxidation of SO_2 by O_3 on the surface of NaCl particles follows a different mechanism [35]. A three-stage mechanism has been proposed: the adsorption of O_3 results in the formation of hydroxide ions; the adsorption of SO_2 occurs on the surface of alkaline NaCl with sulfite as the product; and the sulfite is oxidized to sulfate by O_3 . Under the experimental conditions, the reaction was first order for O_3 and zero order for SO_2 . The adsorption of O_3 on the NaCl surface was the rate-determining step. The reaction order deduced from the proposed mechanism agrees well with the experimental results.

3.3 Organics/ SO_2 -particles reaction under UV illumination

UV illumination will promote the oxidation reaction of organics/ SO_2 on the surface of semiconductor particles. For particles with photocatalytic properties, the reactions of these gaseous pollutants have heterogeneous oxidation mechanisms that are different from those of the homogeneous reactions.

Without UV illumination, the main product of the heterogeneous reactions of formaldehyde on the surface of Al_2O_3 particles is formate, with a small amount of dioxymethylene and polyoxymethylene present together [36, 37]. The reactions on the surface of TiO_2 have similar products [38]. Formaldehyde is first oxidized to dioxymethylene, which is further oxidized to formate. Competitive adsorption occurs between water molecules and formaldehyde on the surface of the particles. Kinetics curves of the formate formation on TiO_2 surfaces with different HCHO concentrations are presented in Figure 7. The reaction of formaldehyde on the surfaces of TiO_2 and Al_2O_3 fit second and first order, respectively. High temperature treatment could enhance the oxidative capacity of the particles. Under atmospheric temperature (troposphere temperature ranges between 200 and 330 K), the uptake rates of formaldehyde molecules increase as the temperature of Al_2O_3 and TiO_2 particles increases. The smaller the particle is and the more active sites per surface area; the surface Al^{3+} and active oxygen species behave as the important active sites in the reactions of formaldehyde on Al_2O_3 particles. The reaction can be accelerated by UV light illumination on the photo-active TiO_2 particles, whereas no UV photocatalytic activity occurs with Al_2O_3 particles [36–38].

The products of the reactions of SO_2 on TiO_2 and ZnO

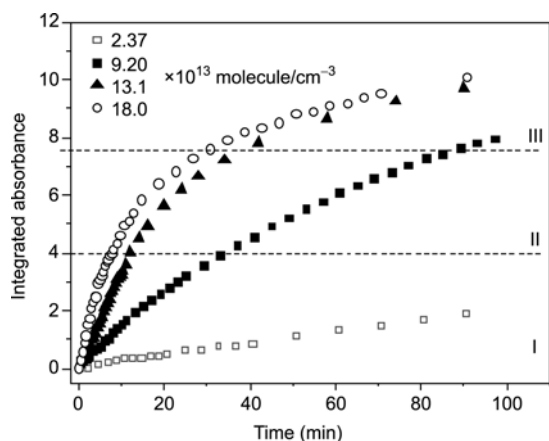


Figure 7 Kinetics curves of formate formation from the TiO_2 particle reactions with different HCHO concentrations. Reactions were conducted at 293 K and the rate of formate formation was determined quantitatively by the integrated absorbance over $1500\text{--}1600\text{ cm}^{-1}$. I, II, and III represent the initial-, transition-, and steady-growth reaction phases, respectively (reproduced from ref. [38], copyrights belong to Science China Press, 2010).

semiconductor surfaces are sulfite and sulfate. A synergistic effect was observed in the production of sulfate when water and UV light were both present. As shown in Figure 8 (reaction of SO_2 on the surface of TiO_2), water or UV illumination alone increased sulfate production; UV had a stronger effect than water. The influence of UV was enhanced significantly in the presence of water and the sulfate production was greater than the sum of sulfate production when water or UV illumination was added separately, revealing a synergistic effect of water and UV illumination on the reaction rate. In the reaction of SO_2 on the surface of ZnO , sulfite was gradually transformed into sulfate with increasing UV irradiation intensity and water vapor. The reaction order and uptake coefficient were calculated on the surface of TiO_2 and ZnO . The uptake coefficient with the presence of water and UV illumination was 1 magnitude higher than that without water and UV illumination. Under

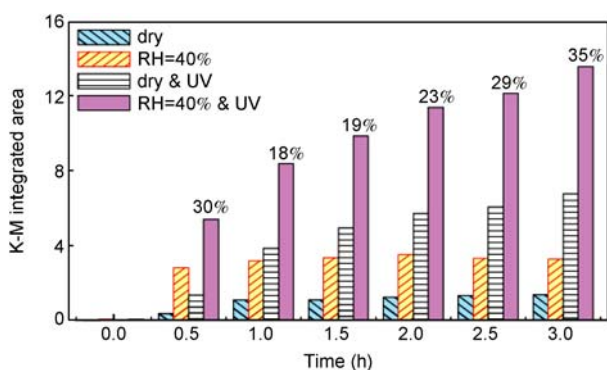


Figure 8 The K-M integrated area of sulfate ($1300\text{--}1100\text{ cm}^{-1}$) under four reaction conditions: dry (without UV), RH=40% (without UV), dry & UV, and RH=40% & UV (reproduced from ref. [40], copyrights belong to Science China Press, 2010).

UV illumination, the photo-generated electrons and holes can react with surface adsorbed oxygen and water, and produce active oxygen species (such as superoxide anions (O_2^-) and hydroxyl radicals ($\cdot\text{OH}$)), which can further oxidize surface-adsorbed SO_2 to produce sulfate [39, 40].

The heterogeneous reactions of organics/ SO_2 on the photocatalytic particles demonstrated that UV illumination in the presence of water vapor enhances the reactive and capability to continue of pollutant gases on the particles. In the real atmospheric environment in which UV illumination and water vapor exist at the same time, the heterogeneous reactions on semiconductor oxides particles may play an important role in the atmospheric chemistry process and should not be ignored.

In summary, we systematically investigated the heterogeneous reactions of important atmospheric gases on representative particulate components and the mechanisms of the air pollution complex based on the microscale reaction kinetics at particle surfaces. Synergetic mechanisms among the ternary reaction systems of NO_2 -particles- H_2O , SO_2 -particles- O_3 , and organics/ SO_2 -particles-UV illumination were identified. These results are of great importance in understanding multiple nonlinear processes at microscale in the atmosphere pollution complex.

4 Heterogeneous reaction processes in the formation of the air pollution complex and gray haze

On the basis of our understanding regarding the heterogeneous reactions on atmospheric particles, we propose a preliminary theoretical model for the formation mechanism of the air pollution complex to describe the coupling mechanism of the formation and transformation of the secondary pollutants in the complex (Figure 9).

In the air pollution complex, heterogeneous reactions on the surface of particles can change the surface composition of the particles and gas phase composition. In the heterogeneous reactions, when three or more factors among the particles, individual reactive gas, relative humidity, and solar irradiation coexist and act together, the reaction process and result are significantly different from that in the presence of only two factors (e.g., particles and one reactive gas species). The synergy underlying this effect is important to elucidate the nonlinear mechanism of the air pollution complex. In addition, atmospheric heterogeneous reactions can increase the oxidation of reducing gases such as NO_x , SO_2 , and HCHO, and produce gaseous oxidants, thereby enhancing the atmospheric oxidation capacity. For example, in the presence of water, the heterogeneous reaction of NO_2 and CaCO_3 can form HONO with a fast rate and increase the OH radical concentration in the atmosphere. O_3 can oxidize SO_2 on the surface of CaCO_3 to form sulfate, and so it plays an important role in the oxidation of SO_2 .

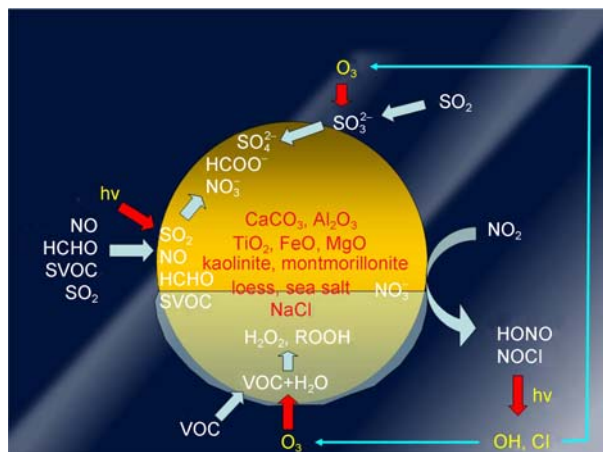


Figure 9 Coupling mechanism for the formation and transformation of the secondary pollutants in the air pollution complex.

The heterogeneous uptake of HCHO on Al_2O_3 and TiO_2 under UV light is a sink for HCHO; thus, it can affect the concentration of HCHO and the concentration of HO_2 in the atmosphere. In the reaction of $\text{SO}_2 + \text{TiO}_2$ or $\text{SO}_2 + \text{ZnO}$, UV light and water synergistically accelerate the reaction, which contributes to the oxidation of SO_2 and formation of sulfate. Meanwhile, these reactions change the composition and hygroscopicity of the particles, which can further alter the reactivity of the gases with the particles.

Besides changing the composition of the gas phase, heterogeneous reactions in the atmosphere also change the composition, light extinction, and cloud condensation nucleation activity of aerosols. Sulfate and nitrate that form in the reaction increase the hygroscopicity of the particles, enhance their size and light extinction efficiency, and thus reduce the atmosphere visibility and accelerate gray haze formation.

Based on the analyses of the synergetic effects in the atmospheric heterogeneous reactions, we propose a conceptual model for the air pollution complex and gray haze formation, as shown in Figure 10.

SO_2 , NO_2 , and the other primary gas pollutants transform to secondary aerosol (e.g., sulfate and nitrate) through heterogeneous reactions on atmospheric particles, which can increase the size and mass concentration of the particles. The change in the composition of the particles enhances their hygroscopicity and increases the water adsorbed on a single particle. For example, $\text{Ca}(\text{NO}_3)_2$, the product of the CaCO_3 reaction with NO_2 , can deliquesce at around 10% RH [26]; this causes the particle to uptake more water and thus increases the particle size and particle surface concentration, further increasing the light extinction of the particle. Moreover, the increased water content can accelerate the gas–liquid–solid reactions of SO_2 and NO_2 on particles, leading to increased hygroscopicity of the particles. Therefore, the above processes form a positive feedback mechanism that enhances the conversion of primary gas pollutants

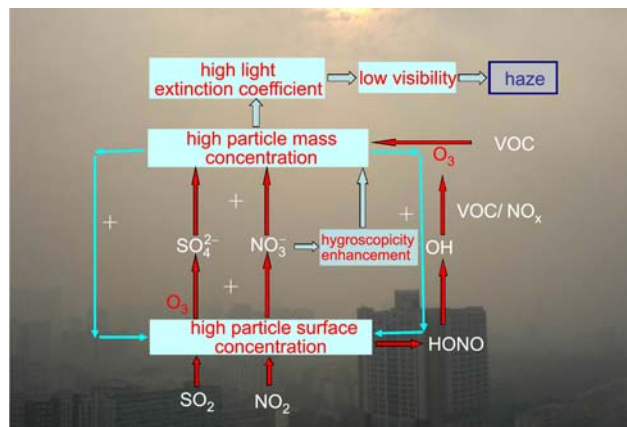


Figure 10 A proposed conceptual model for the formation of the air pollution complex and gray haze.

to secondary aerosols.

Additionally, the heterogeneous reaction of NO_2 on particles produces HONO that can be photolyzed to form the OH radical, which could be an important OH radical source in the atmosphere. The OH radical increases the formation of O_3 through multiple chain reactions involving VOC/ NO_x , and the reaction of VOC with O_3 and OH radical can form secondary organic aerosol (SOA). The acidic sulfate and formate formed through the heterogeneous reactions can increase the formation of SOA and the mass concentration of fine particles [41, 42]. This elevated particle concentration can increase the surface area for the heterogeneous reaction. Therefore, another positive feedback mechanism is formed: the heterogeneous reactions on the particles increase the atmosphere oxidation capacity, which subsequently increases the surface area of particles for heterogeneous reactions, leading to the rapid conversion of primary pollutants to secondary pollutants.

In the air pollution complex, these two positive feedback mechanisms increase the fine particle concentration and enhance the light extinction of particles. Under stagnant meteorological conditions, the accumulation of particles in the atmosphere leads to a rapid increase in light extinction and reduced visibility, thus forming a gray haze.

Ambient RH and its diurnal variation have an important influence on the hygroscopicity and light extinction of particles, therefore affecting the visibility and gray haze formation. Some particle components have a low deliquescence RH and are deliquesced easily in the ambient air. The efflorescence RH is generally lower than the deliquescence RH. At night, the high RH is favorable to particle deliquescence and in the daytime, the particle remains aqueous because the daytime RH may be higher than the efflorescence RH. As a result of the diurnal variation in RH, the particle can keep deliquesced, although the RH in daytime may be lower than the deliquescence point of the particle. Therefore, the particle can maintain a high water content and large light extinction coefficient for a long time. This is likely the reason

why gray haze frequently occurs at low RH.

When the RH is high, many heterogeneous reactions are accelerated; the reaction products can increase the deliquescence and the water adsorption of the particle, thereby accelerating the gray haze formation significantly.

5 Conclusions

The chemical composition and hygroscopicity of atmospheric fine particles determine their environmental effects (radiation/climate, health, ecology) and heterogeneous reactions. Based on systematic laboratory studies on the kinetics and mechanisms of heterogeneous reactions on particle surfaces, we identified synergetic effects of three ternary reaction systems: NO₂-particles-H₂O, SO₂-particles-O₃, and organics/SO₂-particles-UV illumination. The results demonstrate that laboratory studies can help us to understand the coupling mechanism and the nonlinear processes in the formation and transformation of secondary pollutants in the air pollution complex at the molecular level.

Our study found that a layer of sulfate and nitrate, which are highly hygroscopic, formed on the surface of particles during heterogeneous reactions and this enhanced hygroscopicity of the particles can accelerate heterogeneous reactions and increase the extinction coefficient of the particles. This positive feedback mechanism may play an important role in the formation of the air pollution complex, gray haze, and cloud condensation nucleus. Therefore, we propose a conceptual model of the formation of the atmosphere complex, pollution, and haze.

At present, the heterogeneous reactions studies of trace gases and particles remain preliminary, and further investigations should be conducted in the following areas:

(1) Studies on the kinetics of heterogeneous reactions at conditions closer to those of the actual atmospheric environment. This would require increasing the sensitivity of online *in situ* observation instruments and reducing the reactant concentrations as well as studying reactions on particles with the existing form closer to actual atmospheric conditions by carrying out the research using single particles to react with trace gases, developing quantitative methods for heterogeneous reactions on single particles, and establishing the corresponding reaction models. Also, based on the *in situ* observations of particle surface information, one should establish detection methods for real-time monitoring of the concentrations of gaseous reactants and products, study the heterogeneous reactions of atmospheric pollutants on particles under actual atmospheric conditions, and determine free radicals during the reactions to better understand the heterogeneous reaction mechanism.

(2) Identification of more heterogeneous reaction systems with synergetic effects during the reaction, including the reactions of gaseous pollutants on the surface of liquid or solid organic aerosols as well as carbonaceous aerosols;

the reactions of volatile organic compounds on the surface of mineral particles to provide evidence for the formation of secondary organic aerosols; the roles of catalytic reactions of metals especially transition and heavy metals in the heterogeneous reactions; and the influences of environmental factors such as temperature, humidity, UV-vis illumination, and atmospheric oxidants on the heterogeneous reactions.

(3) Application of numerical models and field observations to evaluate the contributions of heterogeneous reactions in the actual atmosphere to the air pollution complex to quantitatively assess the importance of heterogeneous reactions in the atmospheric environment and to systematically elucidate the heterogeneous reaction mechanisms in the formation of the air pollution complex and haze.

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