Observation of Gas-to-Particle Conversion at Low Concentration of SO_2 by Using a Flow-type Reactor

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Particle generation by SO_2 gas-to-particle conversion in a flow-type reactor was examined. The reactor can minimize losses of reactants and products due to adsorption onto the wall surface, and a material balance between consumed SO_2 and sulfate in generated particles was in very good agreement as compared with previous studies.

Atmospheric aerosols which are generated from gaseous species through gas-to-particle conversion processes are of great importance from a viewpoint of global material circulation as well as their impacts on the climate due to the effect of changing albedo.[1] Sulfate is one of the major inorganic components of air-borne particles.[2,3] Aerosols consisting of sulfate play important roles in atmospheric heterogeneous reactions,[4,5] cloud systems,[6,7] etc. There have been many fields, laboratory and theoretical studies on gaseous reactions of atmospheric SO_2 with OH.[8] However, the relationship between aerosols and their precursors (SO_2, OH, etc.) is not clear due to the lack of experimental datas. The production rate of sulfuric acid vapor had an uncertainty of at least one order of magnitude for the SO_2–air–$h\nu$ ($\lambda < 245.4$ nm) system.[9,10] For total particle number concentration of sulfuric acid liquid droplets, several orders of magnitude differences lay in both experimental and theoretical results[10]. The recommendation was given that the amounts of the wall loss and the purity of system should be carefully examined.

Here we report results of laboratory study on the gas-to-particle conversion by using a flow-type reactor, which may provide accurate informations for particle generation rate.

A flow-type reactor for studying SO_2 photooxidation and nucleation processes is schematically illustrated in Figure 1. This reactor was designed with reference to that of Raes et al.[11] They examined NH_4NO_3 aerosol formation by photoirradiation to a gas mixture of NO_2, NH_3 and H_2O in air. However, this type of flow reactor, which depresses the wall loss on the reactor surface, has not been applied to the SO_2 gas-to-particle conversion, so we studied particle generation from low concentration SO_2 using a gas mixture containing SO_2, O_3 and H_2O in air. When the gas mixture is irradiated with 248 nm UV light, O_3 decomposes to $O(^1D)$ and O_2 (reaction 1). No absorption band lies around 248 nm wavelength for SO_2 and O_2 molecules. $O(^1D)$ reacting with H_2O, generates OH radical (reaction 2). $O(^1D)$ also reacts with N_2 and O_2 generating $O(^3P)$ (reaction 3). OH radical and $O(^3P)$ reacting with SO_2 generate H_2SO_4 from oxidized SO_2 (reactions 4, 5). Vapor pressure of H_2SO_4 is very low and liquid droplet particles are generated by H_2SO_4–H_2O system.

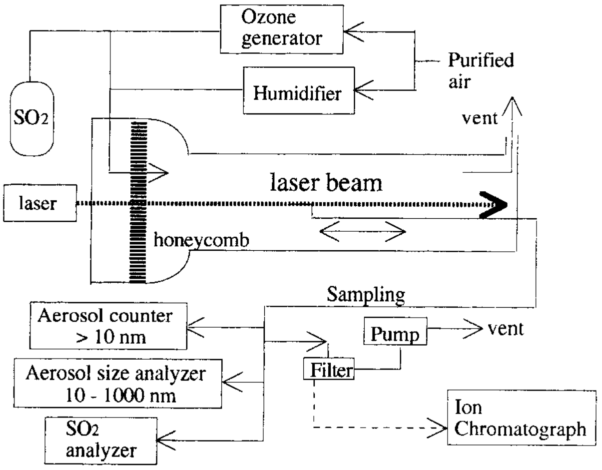

Figure 1. Schematic diagram of the apparatus for photochemical aerosol formation reaction.

The reactor consists of a Teflon honeycomb (356 mm i.d.), to produce a laminar gas flow, and a cylindrical Pyrex glass tube (50 mm i.d.) (Vitro Kagaku) for photoirradiation . The size of eximer laser beam is 1 mm × 1.5 mm. A reaction gas was sampled from the photoirradiated area. The end of a sampling probe is bent to avoid unnecessary irradiation of the reaction gas after sampling. The sampling probe is movable along the center of the flow reactor, which corresponds to different reaction times. An excimer laser (Lambda Physik, MINex 50-L) was used as the 248 nm UV light source. The frequency was 50 Hz and the laser pulse was regarded as a continuous irradiation.

Dilute SO_2 in air cylinder was purchased from Takachiho Kagaku Co. and O_3 was generated from O_2 in air by a UV irradiation method (Ebara OZSD-30UV). Purified air was supplied with a catalytic air purifier (STEC Model SGPU-21). A part of purified air was bubbled through water in a glass bottle to control the humidity of the reaction gas. The reaction gas containing SO_2, O_3 and H_2O vapor was introduced into the reactor and a 248 nm excimer laser beam was irradiating through the vapor near the center of the reaction tube. Total gas flow rate was 5 L/min and all experiments were carried out under atmospheric pressure (Re = 140, laminar flow). The photochemical reactions and particle formations occurred close to the photoirradiated area. This configuration may minimize the loss of reactants and particles due to their adsorption on the reactor wall surface.

The generated aerosols were sampled at different positions of glass tube changing the position of the sampling probe. The number of aerosols was measured with a condensation particle counter (CPC, TSI Model 3022) which can count the particles

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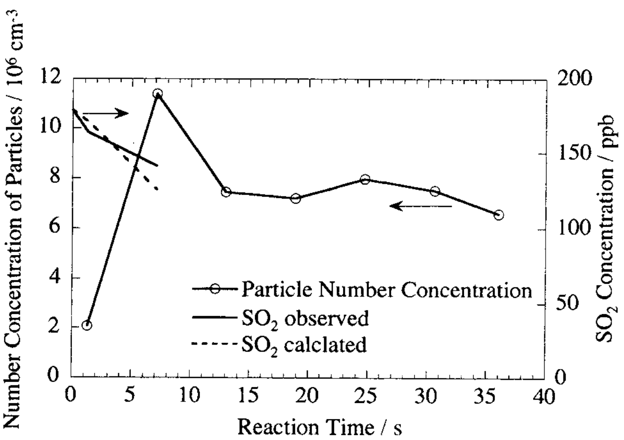

Figure 2. The Change of SO_2 Concentration and Number Concentration of Particles Generated with time under Photoirradiation (SO_2: 179 ppb, O_3: 0.4 ppm, H_2O: 38% RH, 25 °C, 0.2 W/cm²).

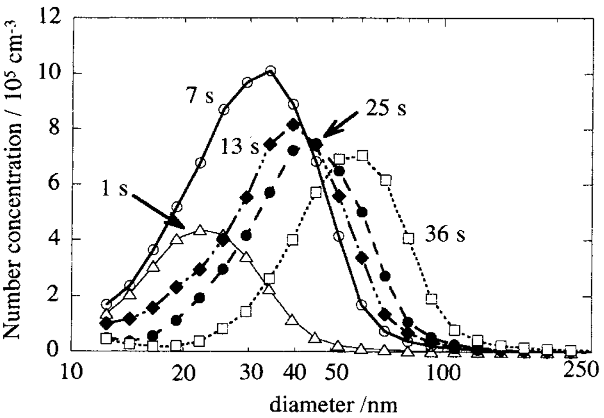

Figure 3. Size Distribution of Particles at Different Reaction Times (SO_2: 179 ppb, O_3: 0.4 ppm, H_2O: 38% RH, 25 °C, 0.2 W/cm²).

larger than 10 nm in diameter. The size distribution of particles from 10 nm to 1000 nm diameter was measured with a scanning mobility particle sizer (SMPS, TSI Model 3934). The SO_2 concentration was measured with a pulsed fluorescent SO_2 analyzer (ThermoElectron, Model 43 S). Sampled gas was diluted with purified air when necessary.

When no UV irradiation was applied, SO_2 concentration remained stable whereas it decreased under photoirradiation (in Figure 2). In our experimental conditions (i.e., initial concentrations of SO_2: 179 ppb, O_3: 0.4 ppm, H_2O: 38% RH, 25 °C, and 0.2 W/cm^2) the amount of SO_2 consumed was 37.6 ppb (21% of initial concentration) within 7 s of reaction time. The decreased amount of SO_2 was calculated to be 8 ppb and 53.0 ppb for 1 s and 7 s reaction time, respectively, using CHEMKIN-II ver. 3.2 (Chemical Kinetics) applied for chemical reaction in laminar gas flow. Reactions 1–5 and reactions of active species with N_2 and O_2 were concerned. At 7 s reaction time, the calculated value was larger than observed one with an error of 29.1%. The gradient of SO_2 concentration between inside and outside the photoirradiated area should be due to the photochemical reaction and the influx of SO_2 from the outside to the inside of photoirradiated area.

The number concentration of particles generated in SO_2–O_3–H_2O–$h\nu$ system is also shown in Figure 2. Particle formation for SO_2–O_3–H_2O system and for O_3–H_2O–$h\nu$ system have been observed (due to remaining NO_x or SO_x in purified air (less than 1 ppb)), but with both systems the particle concentration was low enough to be negligible. Under photoirradiation, aerosol particles were generated immediately. The particle number concentration rapidly increased from 2.1×10^6 cm^{-3} to 1.1×10^7 cm^{-3} from 1 s to 7 s of the reaction time, and then decreased at 13 s.

Particle growth due to coagulation of small particles lead to the decrease of particle number during the reaction. Size distribution of generated particles at different reaction times was thus measured (in Figure 3). The maximum diameter in each size distribution curve was shifted from 20 nm to 60 nm while increasing the reaction time, indicating that the homogeneous particle generation and the particle growth occured. The particle concentration decreased after the peak, but the total volume of the particles increased from 6.4×10^{10} nm^3/cm^3 (1 s) to 1.0×10^{12} nm^3/cm^3 (36 s) during reaction time. The decrease of particle number in Figure 2 can therefore be explained by the particle growth due to the coagulation of small particles.

In this experiment, the material balance of S atoms between consumed SO_2 and sulfate in the particles was 85% and 34% for a reaction time of 1 s and 7 s, respectively. This decrease of the material balance can not be due to the adsorption of sulfate aerosols, but to the diffusion of the aerosols from the photoirradiation zone to dark zone. A calculation, considering the diffusion of reactants and products, is scheduled to estimate a more accurate particle generation rate.

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