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Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate

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Abstract. Sulfate particles play a key role in the air quality and the global climate, but the heterogeneous formation mechanism of sulfates on surfaces of atmospheric particles is not well established. Carbonates, which act as a reactive component in mineral dust due to their special chemical properties, may contribute significantly to the sulfate formation by heterogeneous processes. This paper presents a study on the oxidation of SO_2 by O_3 on $CaCO_3$ particles. Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), the formation of sulfite and sulfate on the surface was identified, and the roles of O_3 and water in oxidation processes were determined. The results showed that in the presence of O_3, SO_2can be oxidized to sulfate on the surface of $CaCO_3$ particles. The reaction is first order in SO_2 and zero order in O_3. The reactive uptake coefficient for SO_2 [$(0.6–9.8)\times10^{14}$ molecule cm^{-3}] oxidation by O_3 [$(1.2–12)\times10^{14}$ molecule cm^{-3}] was determined to be $(1.4\pm0.3)\times10^{-7}$ using the BET area as the reactive area and $(7.7\pm1.6)\times10^{-4}$ using the geometric area. A two-stage mechanism that involves adsorption of SO_2 followed by O_3 oxidation is proposed and the adsorption of SO_2 on the $CaCO_3$ surface is the rate-determining step. The proposed mechanism can well explain the experiment results. The atmospheric implications were explored based on a box model calculation. It was found that the heterogeneous reaction might be an important pathway for sulfate formation in the atmosphere.

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