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Supplement of

Multiphase oxidation of SO_2 by NO_2 on $CaCO_3$ particles

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S1. Deriving the reactive uptake coefficient from aqueous reaction rate constant

The reaction rate constant in the literature was used to derive the reactive uptake coefficient to particles under the same conditions as in this study using the method in Davidovits et al. (2006).

$$\frac{1}{\gamma}=\frac{1}{\Gamma_{diff}}+\frac{1}{\alpha}+\frac{1}{\Gamma_{sat}+\Gamma_{rxn}} \tag{S1}$$

where Γ_{diff} is the transport coefficient in the gas phase, $1/\Gamma_{diff}$ is the resistance due to the diffusion in the gas phase. Similarly, $1/\Gamma_{sat}$ and $1/\Gamma_{rxn}$ are the resistance due to liquid phase saturation and liquid phase reaction, respectively. α is the mass accommodation coefficient of SO_2.

$1/\Gamma_{diff}$ can be derived using the following equation:

$$\frac{1}{\Gamma_{\mathrm{diff}}}=\frac{0.75+0.238\mathrm{Kn}}{\mathrm{Kn}(1+\mathrm{Kn})} \tag{S2}$$

where Kn is the Knudsen number. Knudsen number is defined as

$$\mathrm{Kn}=\frac{\lambda}{a} \tag{S3}$$

where λ is the mean free path of molecule in the gas phase and a is the radius of the particle.

λ can be derived from

$$\lambda=\frac{3D_g}{c} \tag{S4}$$

where D_g is the diffusion coefficient in the gas phase and c is the mean molecular velocity.

c is derived from

$$\mathrm{c}=\sqrt{\frac{8RT}{\pi M}} \tag{S5}$$

where R is the gas constant, T is temperature, and M is the molecular mass of SO_2.

$1/\Gamma_{sat}$ can be derived from

$$\frac{1}{\Gamma_{sat}}=\frac{c}{4HRT}\sqrt{\frac{t\pi}{D_l}} \tag{S6}$$

where H is the Henry constant of SO_2, t is time, and D_l is the diffusion coefficient of SO_2 in the liquid phase.

$1/\Gamma_{rxn}$ can be derived from

$$\frac{1}{\Gamma_{\mathrm{rxn}}}=\frac{c}{4HRT}\sqrt{\frac{1}{k_{rxn}D_l}} \tag{S7}$$

where k_{rxn} is the first order rate constant of the reaction in the liquid phase.

$$k_{rxn}=k[NO_2(aq)] \tag{S8}$$

where k is the second order rate constant of the reaction of S(IV) with NO_2 and $[NO_2(aq)]$ is the NO_2 concentration in the liquid phase.

$$[NO_2(aq)]=H_{NO2}P_{NO2} \tag{S9}$$

where H_{NO2} is the Henry constant of NO_2 and P_{NO2} is the concentration of NO_2 in the gas phase.

S2. Characteristic time for aqueous reaction and gas-particle equilibrium

The characteristic time to achieve the equilibrium in the gas-particle interface and for aqueous reaction of SO_2 with NO_2 were derived using the method in Seinfeld and Pandis (2006).

$$\tau_p \cong \frac{aH^* \sqrt{2\pi MRT}}{3\alpha} \qquad \text{(S10)}$$

$$\tau_{ra} = \frac{1}{k_{rxn}} \qquad \text{(S11)}$$

a is the radius of the particle, H^* is the effective Henry constant, M is the molecular weight, R is the gas constant, T is temperature, α is the mass accommodation coefficient of SO_2. k_{rxn} is the first-order rate constant of the reaction in the liquid phase (see Equation S8). The values of the constants are shown in Table S1.

The characteristic time to achieve the equilibrium in the gas-particle interface is around 4×10^{-5} s. The characteristic time for aqueous reaction is 0.5 and 0.08 s using the reaction rate constant of 2×10^{6} mol^{-1} L s^{-1} (Lee and Schwartz, 1983) and 1.24×10^{7} mol^{-1} L s^{-1} (Clifton et al., 1988), respectively.

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Table S1 Constants used for deriving uptake coefficients from reaction rates and deriving characteristic time

Parameter	**Value**	**Reference**
D_g (m^2 s^{-1})	10^{-5}	-
a (m)	8.3×10^{-6}	-
R (J mol^{-1} K^{-1})	8.314	-
T (K)	298	-
M_{SO2} (Kg mol^{-1})	6.4×10^{-2}	-
α	0.35	Davidovits et al. (2006)
D_l (m^2 s^{-1})	8.3×10^{-12}[a]	Mahiuddin and Ismail (1983)
H_{SO2} (mol L^{-1} atm^{-1})	1.23	Seinfeld and Pandis (2006)
H_{NO2} (mol L^{-1} atm^{-1})	1×10^{-2}	Seinfeld and Pandis (2006)
k (mol^{-1} L s^{-1})	2×10^{6} 1.24×10^{7}	Lee and Schwartz (1983); Clifton et al. (1988)

[a] The aqueous phase diffusion coefficient was derived from the viscosity of $Ca(NO_3)_2$ solution providing that diffusion coefficient is inversely proportional to viscosity according to the Stokes−Einstein equation (Bones et al., 2012) and assuming that the diffusion coefficient in water is 10^{-9} m^2 s^{-1}.

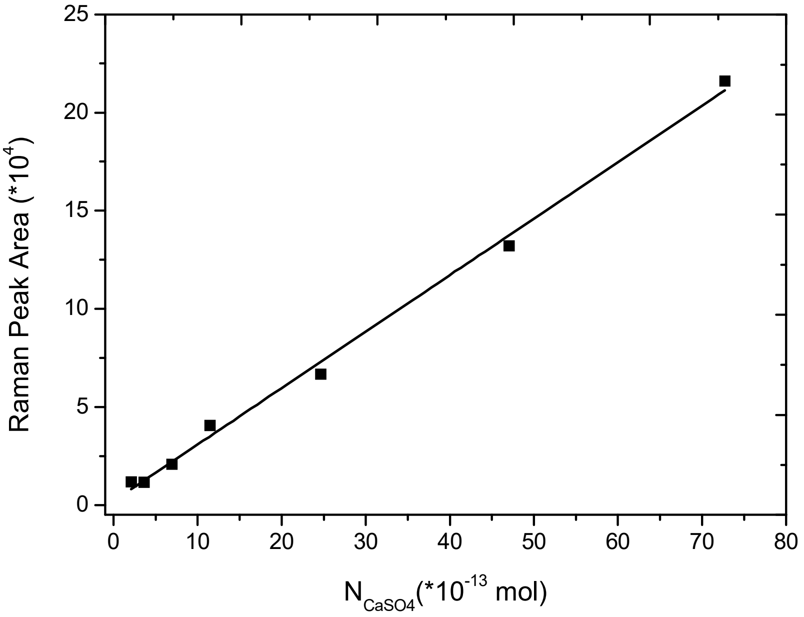

Figure S1. Calibration curve for sulfate showing the peak area of sulfate at 1016 cm^{-1} in Raman spectra versus the amount of $CaSO_4$.

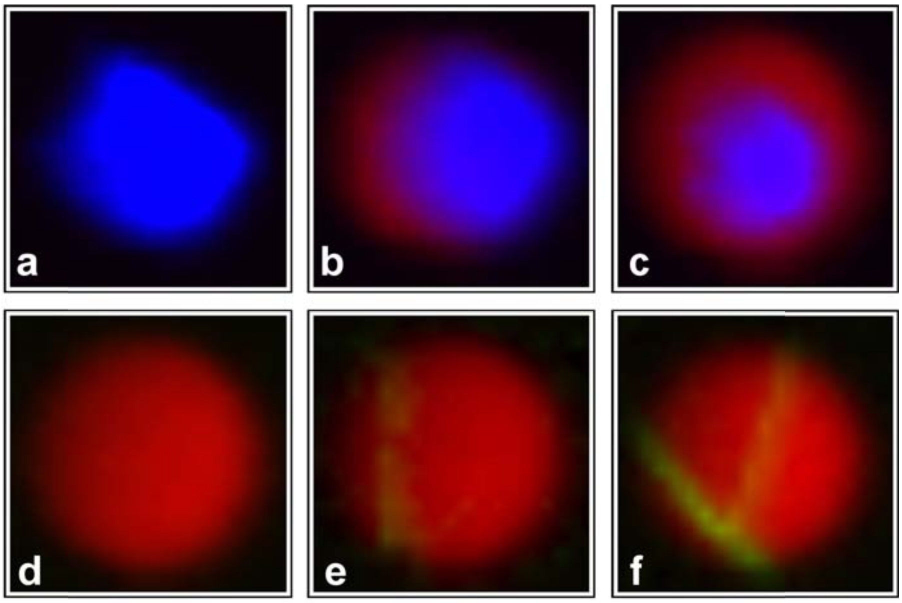

Figure S2. Raman mapping analysis of a $CaCO_3$ particle during the reaction with NO_2 (75 ppm) and SO_2 (75 ppm) at 72% RH at the reaction time of 0, 8, 26, 40, 97, and 1053 min. Blue, red, and green indicate the Raman peak intensity of carbonate, nitrate, and sulfate at 1087, 1050, and 1013 cm^{-1}, respectively.