

The Reactivity of Mineral Dust and Soot Surfaces Towards NO₂, SO₂ and H₂O in the Temperature Range 180 to 670 K

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Abstract

The chemistry of atmospheric aerosol surfaces is currently not well understood. Important remaining questions concern the modification of the aerosol surfaces during ageing, the removal of trace gases from the gas phase and the processing in the hydrological cycle. Mineral dust and soot have been chosen as typical heterogeneous surfaces, which are ubiquitous in the atmosphere, and the role of which is still not very well understood. In this work these surfaces have been characterized in terms of two important issues:

Hydrophilicity of atmospheric surfaces: Hydrophilicity is a critical but difficult to quantify parameter, characterizing the possibility of aerosol particles to act as cloud/ice condensation nuclei. Therefore, adsorption and desorption rates together with the amount of water adsorbed, are important parameters in the assessment of the hydrophilicity. Regarding this issue we have studied the interaction of mineral dust and kerosene soot surfaces with water vapour in the temperature interval $203\text{ K} < T < 298\text{ K}$ using a Knudsen cell reactor. A comparison of the uptake kinetics and adsorption enthalpies of water on mineral dust and soot leads to the conclusion that water is interacting with mineral dust much stronger than with soot. In terms of the hydrophilicity concept the results suggest, that mineral dust may be regarded as hydrophilic whereas soot is hydrophobic and that fundamental kinetic and thermo-chemical parameters may be used to quantify this concept.

Reactivity of atmospheric surfaces: We have investigated two different types of soot samples (kerosene and ethene) and their behaviour towards NO₂ and SO₂ (as typical atmospheric pollutants) in a wide temperature interval between $180\text{ K} < T < 670\text{ K}$. It has been found that under these conditions SO₂ undergoes only reversible adsorption/desorption on the surface, whereas for temperatures above 300 K NO₂ adsorbs irreversibly on the surface and reacts further leading to the formation of NO and HONO as gas phase products with strongly temperature dependent yields. Complementary, for temperatures above 470 K, the formation of CO₂ as gas phase product is observed. For the mechanistic interpretation of the reaction we have found that NO₂ adsorbs irreversibly on the surface, followed by further formation of HONO or reduction to NO (depending on temperature). Additionally, due to the reduction to NO, a new oxidised surface site is formed at higher temperatures, which releases CO₂ into the gas phase, indicating the ability of NO₂ to oxidize the soot sample followed by the consumption of soot.