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Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of α-Al_2O_3 and MgO

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Abstract. Here we compared the heterogeneous reactions of carbonyl sulfide (OCS) on the surface of α-Al_2O_3 and MgO and the effect of water on the reactions at 300 K using Knudsen cell – mass spectrometry, diffuse reflectance infrared Fourier transform spectroscopy, and temperature programmed reactions. H_2S and CO_2 were found to be hydrolysis products of OCS on both α–Al_2O_3 and MgO at ambient temperature. At low water vapor pressure (<6.8×10^{-6} Torr), when water vapor pressure in the Knudsen cell reactor increased from 2.3×10^{-6} to 6.8×10^{-6} Torr, the initial true uptake coefficient of OCS on α-Al_2O_3 decreased from $4.70\pm0.45\times10^{-7}$ to $3.59\pm0.34\times10^{-7}$; while it increased from $5.19\pm0.49\times10^{-7}$ to $6.48\pm0.62\times10^{-7}$ on MgO under the same conditions. At high relative humidity (0.07 – 0.67), the observed uptake coefficients of OCS on α-Al_2O_3 and MgO, which were measured using an in situ DRIFTS, decreased from $4.63\pm0.22\times10^{-6}$ to $1.00\pm0.47\times10^{-6}$ and from $9.72\pm0.46\times10^{-5}$ to $7.68\pm0.36\times10^{-5}$, respectively, when RH increased from 0.07 to 0.67 corresponding to 1.7 – 15.9 Torr of water vapor pressure. In the RH region of 0.17 – 0.67, the average observed uptake coefficient of OCS on α-Al_2O_3 and MgO was equal to $8.34\pm2.19\times10^{-7}$ and $8.19\pm0.48\times10^{-5}$, respectively. The restrictive effect of water on the heterogeneous reaction of OCS on the surface of α-Al_2O_3 and MgO was found to be related to competitive adsorption between water and OCS molecules; while the promotive effect of water on the heterogeneous reaction of OCS on the surface of MgO at low coverage was ascribed to the formation of surface hydroxyl groups. When the environmental RH was greater than the RH of the monolayer, which occurred readily at the atmospherically relevant humidity in the troposphere, thick water layer formed on the mineral dusts, especially, the basic thick water layer formed on the basic component of mineral dusts may be the primary contributor to the heterogeneous hydrolysis of OCS in the troposphere.

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