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Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of α -Al₂O₃ and MgO

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Abstract. Here we compared the heterogeneous reactions of carbonyl sulfide (OCS) on the surface of α -Al₂O₃ 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. H₂S and CO₂ were found to be hydrolysis products of OCS on both α -Al₂O₃ and MgO at ambient temperature. At low water vapor pressure ($<6.8 \times 10^{-6}$ 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 -Al₂O₃ decreased from $4.70 \pm 0.45 \times 10^{-7}$ to $3.59 \pm 0.34 \times 10^{-7}$; while it increased from $5.19 \pm 0.49 \times 10^{-7}$ to $6.48 \pm 0.62 \times 10^{-7}$ on MgO under the same conditions. At high relative humidity (0.07–0.67), the observed uptake coefficients of OCS on α -Al₂O₃ and MgO, which were measured using an in situ DRIFTS, decreased from $4.63 \pm 0.22 \times 10^{-6}$ to $1.00 \pm 0.47 \times 10^{-6}$ and from $9.72 \pm 0.46 \times 10^{-5}$ to $7.68 \pm 0.36 \times 10^{-5}$, 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 -Al₂O₃ and MgO was equal to $8.34 \pm 2.19 \times 10^{-7}$ and $8.19 \pm 0.48 \times 10^{-5}$, respectively. The restrictive effect of water on the heterogeneous reaction of OCS on the surface of α -Al₂O₃ 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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