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Ozone decomposition kinetics on alumina: effects of ozone partial pressure, relative humidity and repeated oxidation cycles

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Abstract. The room temperature kinetics of gas-phase ozone loss via heterogeneous interactions with thin alumina films has been studied in real-time using 254nm absorption spectroscopy to monitor ozone concentrations. The films were prepared from dispersions of fine alumina powder in methanol and their surface areas were determined by an in situ procedure using adsorption of krypton at 77K. The alumina was found to lose reactivity with increasing ozone exposure. However, some of the lost reactivity could be recovered over timescales of days in an environment free of water, ozone and carbon dioxide. From multiple exposures of ozone to the same film, it was found that the number of active sites is large, greater than 1.4×10^{14} active sites per cm^2 of surface area or comparable to the total number of surface sites. The films maintain some reactivity at this point, which is consistent with there being some degree of active site regeneration during the experiment and with ozone loss being catalytic to some degree. The initial uptake coefficients on fresh films were found to be inversely dependent on the ozone concentration, varying from roughly 10^{-6} for ozone concentrations of 10^{14} molecules/ cm^3 to 10^{-5} at 10^{13} molecules/ cm^3 . The initial uptake coefficients were not dependent on the relative humidity, up to 75%, within the precision of the experiment. The reaction mechanism is discussed, as well as the implications these results have for assessing the effect of mineral dust on atmospheric oxidant levels.

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