The Interaction of H$_2$O Vapor with Flame Soot in the Range 193-300K: The Role of Fuel Sulfur

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Owing to the projected phenomenal predictions of sustained growth of global civil aviation at the tune of approximately 6% per year for the next few decades the direct injection of soot aerosol and other exhaust from the jet engines of civil aircraft into the upper troposphere and lower stratosphere begins to be of serious concern to the climate community as far as persistent contrail and Cirrus as well as aviation-induced Cirrus cloud formation is concerned. Sensitivity studies of warm (Cumulus and convective) as well as cold (Cirrus or ice) clouds have revealed that changes in abundance, cloud height, optical density and cloud particle size are parameters that may lead to radiative forcings of either sign many times larger than for CO$_2$, the benchmark for radiative forcing due to a greenhouse gas par excellence. Recent research has shown that soot aerosol is the only likely candidate for providing ice nuclei (IN) in sufficient numbers and at sufficiently high rates of nucleation for contrail formation which is a apparently a very efficient process. This may be visually checked for the case of persistent contrails that are formed in the plume of an aircraft flying at an altitude between 8 and 12 km depending on geographical latitude and at appropriate meteorological conditions. However, up to now there has been a certain reluctance by the scientific community to regard freshly emitted soot aerosol as IN as it is hydrophobic or water-repellent from a macroscopic bulk water point of view.

In addition , the jet exhaust of modern engines contains SO$_x$ (SO$_2$ + H$_2$SO$_4$) species that may interact with the soot aerosol and fundamentally modify its interfacial properties so as to render it hydrophilic. Therefore, ice nucleation in aviation contrails has been postulated to involve H$_2$SO$_4$-coated soot aerosol particles that are formed prior to interaction with water vapor at plume ages between 10 and 30 ms. This implies in turn that the coating process with H$_2$SO$_4$ has to be extremely rapid and should occur on the same time scale so as to provide H$_2$SO$_4$ - coated soot particles ready to adsorb H$_2$O vapor that will ultimately lead to the generation of ice particles constituting the rectilinear clouds known as aviation contrails. In this work we are going to examine two questions from an experimental point of view: (a) is a H$_2$SO$_4$ - coating of soot substrates necessary for adsorption of H$_2$O molecules which may be considered as the first step of ice nucleation? (b) How much sulfuric acid does one in fact find to be adsorbed on soot at a given fuel sulfur content (FSC)? We propose to use a surrogate albeit well-defined flame soot

generated in the laboratory using a reproducible diffusion flame sustained by the combustion of hexane, octane and decane at two limiting conditions, namely a near-stoichiometric (grey soot) and lean (black soot) diffusion flame.

The interaction of H_2O vapor with laboratory soot generated from the controlled combustion of decane has been examined on a molecular basis by using a novel real-time experimental technique based on the molecular diffusion of H_2O across a tube coated with the soot of interest and recording the arrival time of H_2O using time-dependent mass spectrometry. The arrival time across the soot coated tube is compared to the one resulting from the diffusion across a non-interacting Teflon-coated reference tube. A Monte-Carlo model based on the superposition of individual molecular trajectories is used to obtain three parameters controlling the H_2O-soot interaction, namely the uptake coefficient γ, the surface residence time τ_{surf} of H_2O adsorbed on the two different types of soot (grey and black) and the number of adsorption sites n_s for H_2O adsorption on soot. The temperature dependence of τ_{surf} which is the inverse of the absolute values for the rate constant for desorption of H_2O from soot obtains the Arrhenius activation energy of desorption which leads to the enthalpy of adsorption of adsorbed H_2O. The three kinetic parameters as well as the enthalpy for H_2O adsorption on soot (grey and black) describe the water vapor/soot interaction from a fundamental point of view in the initial stages of water adsorption. The H_2O adsorption kinetics depend on the type of soot. The heat of adsorption of H_2O on decane soot varies from 7 (grey) to 9 (black soot) kcal/Mol compared to 12.3 kcal/Mol for H_2O evaporation from thermodynamically stable hexagonal ice.

When the nominally S-free "pure" decane hydrocarbon fuel is spiked with up to 500 ppm of thiophene (C_4H_4S) the resulting soot from a diffusion flame has water adsorption properties that are indistinguishable from soot obtained using unspiked decane. As a baseline experiment we have performed extraction of grey decane soot in methanol obtained from the combustion of "pure" decane. It indicated an upper limit of 3.4×10^{-4} and 4×10^{-4} of a formal monolayer of sulfate (ion chromatographic detection) and total S (ICP analysis), respectively. We conclude that "pure" decane of unspecified S-content does not lead to adsorbed sulfur accumulation, either as sulfate or as some other form of adsorbed S that may support the H_2O adsorption on soot. The comparison of the kinetic results (γ, τ_{surf}, n_s) between "pure" and S-spiked decane soot suggests neglibible sulfate content of soot in the examined range of 50 and 500 ppm.

In order to systematically investigate the sulfate-content of soot obtained from the combustion of spiked vs. pure hydrocarbon fuel both grey and black hexane and octane fuel have been combusted with increasing FSC going from 0 to 5000 ppm (v/v) using the CAST. Owing to the liquid nature of the fuel it

has been vaporized prior to diffusion mixing and combustion in the CAST in contrast to standard use of gaseous fuels. Thiophene/N_2 vapors have been combined with the fuel/N_2 mixture upstream of the combustion zone in order to preserve full flexibility in the mixing ratio. Soot from a near-stoichiometric (λ (fuel-to-oxygen ratio) = 0.84) and lean (λ = 0.2) diffusion flame has been collected, extracted in methanol and investigated regarding its sulfate content using ion chromatography. Up to mixing ratios of 500 ppm of thiophene small amounts of sulfate are found to be adsorbed on both hexane and octane soot. On grey hexane and octane flame soot 0.2 and 0.06% of thiophene, respectively, are found as adsorbed sulfate whereas the corresponding numbers for black hexane and octane soot are 0.3 and 0.07%, respectively. At 5000 ppm_v of thiophene the conversion efficiencies are 0.6 and 0.03% for grey hexane and octane, respectively, and 0.14 and 0.05% for black hexane and octane soot, respectively. These numbers are well below 1% over all conditions sampled and imply that H_2SO_4, if formed in the early plume at all, is not deposited onto the emitted soot under the present conditions of a diffusion flame. The overwhelming majority of S certainly is emitted as SO_2 with generally a 2-4% conversion to H_2SO_4 of which a small fraction ends up as adsorbed H_2SO_4 except perhaps for grey hexane soot with up to 1% of FSC as adsorbed sulfate. Apart from the maximum case of grey hexane soot for which peak efficiencies of FSC to adsorbed sulfate of 0.82% have been recorded, the corresponding numbers remain below 0.3% for black hexane soot and below 0.1% for octane soot. It seems that H_2SO_4 adsorption is favored for hexane compared to octane soot, presumably owing to a smaller mode of the soot particle size distribution function for hexane fuel, especially for near-stoichiometric combustion conditions ($\lambda = 0.8$ or grey soot).

In conclusion, we have shown that efficient H_2O adsorption at atmospherically relevant temperatures (190 to 300K) onto laboratory flame soot whose properties are closely controlled does not depend on the existence of adsorbed H_2SO_4 which is not to say that adsorption may take place as efficiently in the case of a H_2SO_4-coated soot particle. Apparently, there are always surface sites for H_2O adsorption present in sufficient numbers that may correspond to oxidized sites or surface-OH functionalities on the soot substrate. Quantitatively, the energy of interaction for H_2O interacting with soot corresponds to 50-75% of the sublimation energy of H_2O from crystalline ice. The hydrophobic nature of freshly emitted soot is certainly misplaced in this case as we investigate the interaction of the H_2O-soot pair from a molecular as opposed to a bulk point of view. Soot samples generated from a laboratory diffusion flame of hexane and octane do not show significant accumulation of adsorbed H_2SO_4 with increasing FSC content from 0 to 5000 ppm, regardless of combustion conditions. This result should be verified in the field on authentic samples of aviation soot.