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# Adsorption of nitrogen and water vapor by insoluble particles and the implication on cloud condensation nuclei activity

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ABSTRACT

The adsorption parameters of three insoluble species, black carbon, kaolinite and montmorillonite particles were measured using an accelerated surface area and porosimetry system with nitrogen and water molecules as adsorbates to estimate the ability of insoluble species to act as cloud condensation nuclei (CCN). The surface area of adsorbents was determined using the Brunauer–Emmett–Teller (BET) isotherm analysis and further incorporated in Frenkel–Halsey–Hill (FHH) isotherm analysis to illustrate the multilayer adsorption process at high saturation conditions. The derived BET adsorption parameters suggest a higher multilayer adsorption at surface coverage ($\theta$)=1 for water adsorption than $N_2$ adsorption, i.e., $24 \pm 2\%$ vs $8 \pm 3\%$. The water adsorption on carbon surface showed no consistent trend for the BET isotherm possibly due to the hydrophobic properties. However, for water saturation ($S$) in the range of 0.4–0.9, all three components followed a good FHH isotherm trend. The required supersaturation ($SSc$) to form CCN using the FHH-adsorption activation theory showed a lower criterion for montmorillonite by 0.05–0.3% than that for black carbon and kaolinite. The equivalent hygroscopicity parameters, $\kappa$, was estimated as $\sim$0.002 for montmorillonite and less than 0.001 for both black carbon and kaolinite at a dry diameter of 200 nm. The results suggested that montmorillonite is a better CCN than the other two species. In addition to the adsorption parameter determination, the surface coverage was revised using the original definition and showed a higher required supersaturation than the simplified formula which was applied in earlier studies. Such deviation is more significant for composition having higher hygroscopicity and suggests the possible overestimation of CCN activation using the simplified equation, commonly applied in most studies.



## 1. Introduction

Aerosol particles play an important role influencing human life such as acting as pollutants affecting human health, scattering or absorbing radiation (IPCC, 2013; Seinfeld & Pandis, 2006) affecting climate directly or as cloud condensation nuclei (CCN) varying the cloud albedo and the hydrological cycle (Facchini, Mircea, Fuzzi, & Charlson, 1999; Lohmann & Feichter, 2005; Murphy, 2005; Tunved et al., 2006; Twomey, 1974, 1977). The impact of aerosol particles on human's life is strongly dependent on the physicochemical properties of the particles (Martin, 2000). In IPCC report (2013), the ability of aerosol particles affecting the cloud albedo

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has a significant uncertainty partially due to the strong composition variation temporally and spatially, as the ability of aerosols activating into cloud drops depends strongly on their dry size and composition. Activation of soluble particles in the atmosphere is relatively easy due to the well-known solute effect that can drastically depress the droplets' surface vapor pressure. As to the insoluble aerosol species such as dust particles, they are often thought to be hydrophobic and thus can only influence cloud by acting as ice nuclei to initiate cloud glaciation. However, recent studies indicated that they might also serve as cloud condensation nuclei through a different mechanism such as the adsorption processes (Kumar, Sokolik, & Nenes, 2011a, 2011b; Sorjamaa & Laaksonen, 2007).

The water adsorption process on the insoluble particles without solute effect was generally described by the adsorption-activation theories such as Brunauer–Emmett–Teller (BET) isotherm applied for surface area analysis (Brunauer, Emmett, & Teller, 1938; Henson, 2007) or Frenkel–Halsey–Hill (FHH) isotherm commonly used to describe the multilayer adsorption (Carrott, McLeod, & Sing, 1982; Halsey, 1948; Hill, 1952; Kumar, Sokolik, & Nenes, 2009). Due to the lower free surface energy on the insoluble particles than the gas molecule clusters, the insoluble particles can enhance the cloud droplet formation (Brunauer et al., 1938). The water adsorption on the insoluble particles were studied using different techniques, such as FT-IR (Hatch, Greenaway, Christie, & Baltrusaitis, 2014; Hatch et al., 2012) to monitor the IR spectral variation of water adsorption and further to derive the isotherm parameters. Another approach is using a cloud condensation nuclei counter (Kumar et al., 2011a, 2011b) to measure the required critical diameter as a function of supersaturation which was then used to characterize the interaction between particle water molecules in BET or FHH isotherm (Kumar et al., 2009, 2011a, 2011b). Possibly due to the difference between experimental methods and the sample preparation, there is deviation among the results which require further investigation.

In this study, the adsorption parameters ($C_{BET}$, $A_{FHH}$ and $B_{FHH}$) for three common atmosphere related insoluble samples were derived based on the adsorption profiles as a function of gas saturation using a physisorption analyzer with nitrogen and water vapor as adsorbates. The isotherm parameters were applied to discuss the coverage behavior and the interaction of the adsorbent surface and adsorbate molecules. The droplet growth as a function of the water saturation based on the derived adsorption parameters were further applied to estimate the required critical supersaturation (*SSc*) to act as cloud condensation nuclei (CCN) which were compared with other studies. The impact of parameter accuracy and the revised surface converge on the particle activation were discussed.

## 2. Experimental methods and data analysis

### 2.1. Experimental methods

In this study, two adsorbates were applied: nitrogen for the determination of the adsorbent surface area and water vapor for the adsorption behavior at high saturation region to derive the required saturation condition for the CCN activation. The adsorption processes on three common insoluble compositions were measured using an accelerated surface area and porosimetry system (Micromeritics ASAP 2020). Black carbon (Alfa Aesar, 99.9+%, with reported surface area of 72 $m^2\ g^{-1}$), kaolinite ($Al_2Si_2O_5(OH)_4$, Fluka) and montmorillonite K10 power (Sigma Aldrich) were used as received without further purification. The sample powder was placed in an evacuated sample tube to be degassed at 110 °C under vacuumed condition for at least 6 h to remove any pre-adsorbed molecules. The tube was then cooled to a desired temperature for adsorption experiment such as −196 °C for $N_2$. The gas adsorbed was measured by controlling the gas pressure at a series of precisely controlled pressures. With each incremental pressure step, the number of the gas molecules adsorbed on the surface of the sample increased and monitored. The pressure at which adsorption equilibrium occurs was measured and the ideal gas law was applied to determine the quantity of the gas adsorbed. After the nitrogen adsorption experiment, the same sample without further treatment was applied to measure the adsorption behavior of water molecules at 28 °C.

### 2.2. Data analysis

The surface coverage as a function of saturation ratio for BET isotherm is described using an approximation form described as follows (Brunauer et al., 1938):

$$\theta = \frac{C_{BET}S^*(1-(n+1)S^{*n}+nS^{*(n+1)})}{(1-S^*)\left(1+(C_{BET}-1)S^*-C_{BET}S^{*(n+1)}\right)} \sim \frac{C_{BET}S^*}{(1-S^*)(1-S^*+C_{BET}S^*)} \tag{1}$$

where $S^*$ is the saturation of applied adsorbate molecule, $\theta$ is the surface coverage, $C_{BET}$ is the adsorption parameter and $n$ is the number of allowed layer. The simplified approximation form in Eq. (1) is generally valid for $0.05 < S^* < 0.35$ as the multimolecular layers on an adsorbent were considered (Brunauer et al., 1938). As to FHH, saturation can be expressed as a function of $\theta$ with two adsorption parameters; $A_{FHH}$ and $B_{FHH}$ as follows:

$$S^* = \exp\left(-\frac{A_{FHH}}{\theta^{B_{FHH}}}\right) \tag{2}$$

FHH isotherm is generally restricted to $\theta > 2$ to consider the adsorption of adsorbate molecules on a nonporous, nonpolar adsorbent, so Eq. (2) is valid for high saturation region, i.e., a usual applied range of $0.4 < S^* < 0.9$ (Hill, 1952). The adsorption parameters such as $C_{BET}$, $A_{FHH}$ and $B_{FHH}$ are obtained through experimental measurements. If the Kelvin effect is taken into account,