Cloud condensation nuclei activity of CaCO$_3$ particles with oleic acid and malonic acid coatings

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Abstract. Condensation of carboxylic acids on mineral particles leads to coatings and impacts the particles’ potential to act as cloud condensation nuclei (CCN). To determine how the CCN activity of mineral particles is impacted by carboxylic acid coatings, the CCN activities of CaCO$_3$ particles and CaCO$_3$ particles with oleic acid and malonic acid coatings were compared in this study. The results revealed that small amounts of oleic acid coating (volume fraction ($\nu_f$) $\leq$ 4.3%) decreased the CCN activity of CaCO$_3$ particles, while more oleic acid coating ($\nu_f$ $\geq$ 16%) increased the CCN activity of CaCO$_3$ particles. This phenomenon has not been reported before. In contrast, the CCN activity of CaCO$_3$ particles coated with malonic acid increased with the thickness of the malonic acid coating ($\nu_f$ = 0.4–40%). Even the smallest amounts of malonic acid coating ($\nu_f$ = 0.4%) significantly enhanced the CCN activity of CaCO$_3$ particles from $\kappa$ = 0.0028 $\pm$ 0.0001 to $\kappa$ = 0.0123 $\pm$ 0.0005. This indicates that a small amount of water-soluble organic acid coating may significantly enhance the CCN activity of mineral particles. The presence of water vapor during the coating process with malonic acid additionally increased the CCN activity of the coated CaCO$_3$ particles, probably because more CaCO$_3$ reacts with malonic acid when sufficient water is available.

1 Introduction

Atmospheric aerosols serve as cloud condensation nuclei (CCN) and change the radiative properties (cloud albedo effect) and lifetime (cloud lifetime effect) of clouds, thus affecting the Earth’s climate indirectly (Liu and Wang, 2010; Gantt et al., 2012; Penner et al., 2004; Haywood and Boucher, 2000). Mineral aerosol is one of the most abundant components of the atmospheric aerosol. It is estimated that 1500–2600 Tg of mineral aerosol particles with radii between 0.1 and 8 µm are emitted annually into the atmosphere on a global scale (Cakmur et al., 2006). Mineral aerosol particles are mainly composed of substances that are slightly soluble or insoluble in water. CCN activity measurements show that the hygroscopicity parameter $\kappa$ (Petters and Kreidenweis, 2007) varies between 0.001 and 0.08 for mineral aerosols, including CaCO$_3$ aerosol, clay aerosols, and mineral dust aerosols generated in the laboratory or sampled from various locations worldwide (Garimella et al., 2014; Yamashita et al., 2011; Zhao et al., 2010; Koehler et al., 2009; Sullivan et al., 2010; Herich et al., 2009). The low $\kappa$ indicates that the CCN activity of mineral aerosol is much lower than that of water-soluble salts like (NH$_4$)$_2$SO$_4$ ($\kappa$ = 0.61) and NaCl ($\kappa$ = 1.28), which are also common in atmospheric aerosols (Petters and Kreidenweis, 2007). Tang et al. (2016) reviewed recently the interaction of mineral dust particles with water.

Mineral aerosol particles can be coated by organic vapors during their residence and transport in the atmosphere. Many individual particle measurements have shown that mineral components and organic matter can coexist in the
same individual aerosol particle in the real atmosphere (Falkovich et al., 2004, 2001; Russell et al., 2002; Li and Shao, 2010). Carboxylic acids (R(C=O)OH) are abundant species among the organic matter that coexists with mineral particles. Russell et al. (2002) found that carbonyls (R(C=O)R), alkanes, and R(C=O)OH are present in individual mineral (and sea salt) aerosol particles, with enhanced concentration of R(C=O)OH. They also found that Ca$^{2+}$, CO$_3^{2-}$, R(C=O)OH, and R(C=O)R coexisted in some individual mineral aerosol particles with a strong correlation between CO$_3^{2-}$ and R(C=O)OH. These particles could be formed by CaCO$_3$ particles (partly) coated with organic film. Falkovich et al. (2004) also found that organic and inorganic components coexisted in individual mineral aerosol particles with the organic component consisting of various short-chain (C$_1$–C$_{10}$) mono- and dicarboxylic acids (MCA and DCA). The concentration of short-chain carboxylic acids in mineral aerosol particles increased with the increase of the ambient relative humidity (RH). A possible explanation for such observations could be that when more water is condensed onto mineral particles at higher ambient RH, the adsorbed carboxylic acids are ionized in the aqueous environment and react with mineral particles forming organic acid salts. Of the major components of mineral aerosol particles (clay, calcite (CaCO$_3$), quartz, mica, feldspar, etc.), only CaCO$_3$ with alkaline character can react with carboxylic acids in this way. Thus CaCO$_3$ may play a key role in the uptake of carboxylic acids by mineral aerosol particles.

Carboxylic acid coatings on mineral aerosol particles change their chemical composition and thus may have an impact on their CCN activity. Many previous studies have investigated the CCN activity of pure mineral aerosol (Garimella et al., 2014; Yamashita et al., 2011; Zhao et al., 2010; Koehler et al., 2009; Sullivan et al., 2010; Herich et al., 2009) and pure carboxylic acid aerosol (Kumar et al., 2003; Horii et al., 2003; Cruz and Pandis, 1997; Hartz et al., 2006), but only a few studies have investigated the CCN activity of mineral aerosol particles with carboxylic acid coatings (Tang et al., 2015; Hatch et al., 2008; Gierlus et al., 2012).

In this study we used malonic acid (MA) and oleic acid (OA) as coating materials and CaCO$_3$ particles as cores and investigated the CCN activity of the coated CaCO$_3$ particles. Herein we varied the coating thickness and the RH during the coating process. MA is a representative of the class of DCA acids and OA is an example of surfactant-like compounds. DCA acids are ubiquitous in the atmosphere (Kawamura et al., 1996; Kawamura and Ikushima, 1993; Ho et al., 2007; Mkoma and Kawamura, 2013). OA, which is emitted into the atmosphere by the cooking of meat, wood burning, and automobile sources (Schauer et al., 1999; Rogge et al., 1998, 1993), is present in atmospheric aerosols of urban, rural, and forest areas (Cheng et al., 2004; Ho et al., 2010). The water solubility of the two organic acids is complementary; it is high for MA while it is very low for OA. Coatings of MA and OA could thus have different effects on CCN activity of mineral particles.

**2 Experimental**

As general procedure, CaCO$_3$ aerosol was generated according to Zhao et al. (2010), and then poly- or monodisperse CaCO$_3$ aerosol particles were coated with malonic or oleic acid in a coating device. A flow tube was optionally applied to extend the residence time. The particle size, chemical composition, and CCN activity of the CaCO$_3$ particles were measured before and after coating. Figure 1 shows the schematic of the experimental setup.
2.1 Generation of CaCO$_3$ aerosol

CaCO$_3$ aerosol was generated by spraying a saturated Ca(HCO$_3$)$_2$ solution. A sample of CaCO$_3$ powder (2 g, pro analysis, ≥ 99 %, Merck, Darmstadt, Germany) was suspended in 1 L Milli-Q water (18.2 MΩ cm, TOC < 5 ppb). Then about 1.5 L min$^{-1}$ CO$_2$ (purity ≥ 99.995 %, Praxair Industriegase GmbH & Co. KG, Magdeburg, Germany) was bubbled into the suspension at room temperature (RT) for 3 h, while the suspension was stirred using a magnetic stirrer. During bubbling, CO$_2$ reacted with CaCO$_3$ to produce Ca(HCO$_3$)$_2$. After bubbling, the suspension was allowed to settle for 10 min, the supernatant clear Ca(HCO$_3$)$_2$ solution was decanted and used for spraying by a constant output atomizer (model 3076, TSI, Shoreview, MN, USA) using 1.75 L min$^{-1}$ high-purity N$_2$ (Linde LiPur 6.0, purity 99.9999 %, Linde AG, Munich, Germany).

The major portion (0.9 L min$^{-1}$) of the aerosol flow generated by spraying was dried in a diffusion drier filled with silica gel. The RH was below 10 % after drying. The remainder of the aerosol flow was drawn off by a pump and discarded. The dry aerosol was passed through a tube furnace (model RS 120/1000/12, Nabertherm GmbH, Lilienthal, Germany) set at 300 °C. The residence time of the aerosol in the furnace was 5.2 s. Zhao et al. (2010) described this method for generating CaCO$_3$ aerosol in detail. At room temperature, dry Ca(HCO$_3$)$_2$ is thermodynamically unstable and decays into CaCO$_3$, CO$_2$, and H$_2$O (Keiser and Leavitt, 1908). With this method the aerosol still contained some Ca(HCO$_3$)$_2$ after drying, but after heating at 300 °C it was completely converted into CaCO$_3$ (Zhao et al., 2010). The CaCO$_3$ aerosol generated was either first size selected by a differential mobility analyzer (DMA, TSI 3081) with a neutralizer on the inlet or entered the coating device directly as polydisperse aerosol.

Figure 2a shows the total number concentration and mean size of the bare CaCO$_3$ aerosol particles generated at different spraying time, which were measured with the scanning mobility particle sizer (SMPS) described below. The mean size stabilized after about 50 min in the range 49.8–55.5 nm. Over the 232 min spraying time, the total number concentration varied in the range $1 \times 10^6$–$4.5 \times 10^6$ cm$^{-3}$. The total number concentration decreased by about one-third in the initial 70 min. The decrease became slower after 70 min and the total number concentration tended to stabilize after 155 min. After 70 min the total number concentration varied in a smaller range of $1.8 \times 10^6$–$2.9 \times 10^6$ cm$^{-3}$; therefore, the measurements in this study typically started after 70 min spraying. The typical size distribution of the CaCO$_3$ aerosol particles after 70 min spraying is shown in Fig. 2b. The CaCO$_3$ particles showed a single mode distribution with a mode diameter at 32.2 nm. The number concentration was more than $10000$ cm$^{-3}$ for particles between 12.6 and 151.2 nm.

2.2 Organic acid coating

The coating device (Fig. 1b) used in this study was designed by Roselli (2006) and showed good reproducibility, controllability, and stability. The glass apparatus consisted of a small storage bulb (100 mL) holding the organic coating substances which was directly connected to a mixing cell (about 35 mL). The storage bulb and mixing cell were fully immersed in a flow-through water heater connected to a thermostatic bath (F25, Julabo GmbH, Seelbach, Germany). The temperature range of the thermostatic bath used in this study was 30–80 °C. An extra N$_2$ stream could be passed through the storage bulb in order to enhance the organic vapors flowing into the mixing cell. The outflow of the coating device was connected to a Liebig type water cooler. The water cooler was controlled by another thermostatic bath (F25, Julabo GmbH, Seelbach, Germany) operated at 25 °C throughout all of the experiments.

The bottom of the storage bulb was filled with either 5.0 g MA powder (assay ≥ 98 % (T), Fluka Chemika, Sigma-
A flow of 0.9 L min\(^{-1}\) high-purity \(\text{N}_2\) was used to carry the organic acid vapor up into the mixing cell. The flow of 0.9 L min\(^{-1}\) \(\text{CaCO}_3\) aerosol was passed through the mixing cell and mixed with the 0.9 L min\(^{-1}\) \(\text{N}_2\) flow carrying the organic acid vapor. The mixed flow then entered the water cooler. The organic acid vapor was condensed on \(\text{CaCO}_3\) aerosol particles in both the mixing cell and the water cooler. The residence time of the aerosol in the coating device including the cooler was about 6 s. Three identical coating devices, with the same heating and cooling thermostatic bath, were used: one for MA coating, one for OA coating, and a blank one without organic acid for assessing the impact caused by heating the \(\text{CaCO}_3\) aerosol in the coating device without organic acid (Roselli, 2006).

The aerosol could enter the measuring instruments directly or after passing through a flow tube to increase its residence time. The flow tube was made of a straight circular glass tube with a 2.5 cm internal diameter. The aerosol flow in the flow tube was laminar flow. The average residence time of the aerosol in the flow tube was 23.7 s.

For the coating process we mixed flows of 0.9 L min\(^{-1}\) of dry \(\text{N}_2\) and of aerosol dried to < 10 % RH at RT. As a consequence RH at the outlet of the coating device was < 5 % at RT. To investigate the impact of water on the coating process and CCN activity, organic coating at a higher RH was also performed. For that a bubbling device filled with Milli-Q water was utilized to saturate the \(\text{N}_2\) stream with water vapor before it entered the storage bulb (RH > 90 % at RT). After mixing with the aerosol stream at RH < 10 %, the water concentration in the mixing cell corresponded to RH ≈ 50 % at RT or a partial pressure of ≈ 1500 Pa. The RH of the aerosol at the outlet of the coating device at RT was indeed ~ 47 % when humidification was applied. For the partial water vapor pressure of 1500 Pa we calculated RH > 7 % at 60 °C (for MA) and RH > 3 % at 80 °C (for OA), which is about an order of magnitude higher than RH in the dry cases. In fact RH will be somewhat higher as the gas phase may not reach the bath temperature, which primarily serves to warm up the coating agent and control its vapor pressure.

### 2.3 Size and chemical composition measurements

The number size distribution of the aerosol particles was measured using a SMPS (TSI 3080 Electrostatic Classifier with TSI 3081 DMA, TSI 3786 UWPC). The sample flow was set to 0.6 L min\(^{-1}\) and the sheath flow was set to 6.0 L min\(^{-1}\). The size range measured was 9.82–414.2 nm with a size resolution of 64 channels per decade and the time resolution was 3 min for a complete scan. Despite the maximum resolution of the SMPS the size bin width was still substantial compared to the observed growth by coating. We therefore derived the diameter of the coated (and the respective bare \(\text{CaCO}_3\) particles) by interpolating in between the size bins. For that we considered 5–9 size bins around the size bin of nominal mode and fitted a lognormal distribution to these data. The fitted mode positions are listed in Table 1. The error bars in x direction in Fig. S1 in the Supplement show the shifts of the fitted mode position relative to the nominal size bin.

The chemical composition and the vacuum aerodynamic diameter of the aerosol particles were measured using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., Billerica, MA, USA; DeCarlo et al., 2006). The aerosol particles were vaporized at 600 °C and ionized by electron impact ionization at 70 eV; i.e., we focused on the measurements of the organic coatings and sacrificed a direct \(\text{CaCO}_3\) determination by AMS (compare Zhao et al., 2010). The AMS was routinely operated in V mode in two alternating modes: 1 min MS mode to measure the chemical composition and 2 min PToF mode. Only MS mode data were analyzed. AMS measurements and SMPS measurements were synchronous and both were repeated at least four times for each sample. Size information for bare \(\text{CaCO}_3\) was taken from SMPS data in the blank coating device.

We used specific marker \(m/z\) to derive the amount of organic coating. For pure oleic acid the signal at \(m/z\) 41 (\(\text{C}_3\text{H}_7^+\)) was reported to be the strongest signal in the mass spectrum measured by Q-AMS at EI energy of 70 eV and vaporizer temperature of 600 °C (Sage et al., 2009). The signal at \(m/z\) 41 was also strongest for OA coatings in our HR mass spectra. In order to get a high signal-to-noise ratio we choose the signal at \(m/z\) 41 in the MS mode of the AMS measurement as a marker for OA in the coated \(\text{CaCO}_3\) particles. There was no significant signal at \(m/z\) 41 for the uncoated \(\text{CaCO}_3\) particles. The average background signal at \(m/z\) 41 per single aerosol particle corresponded to 2.7 ± 0.9 × 10\(^{-12}\) µg for bare \(\text{CaCO}_3\). The average value presented the baseline of the mass spectra and the standard deviation (SD) was derived from the noise of the mass spectra at \(m/z\) 41. Similarly, the signal at \(m/z\) 42 (\(\text{C}_2\text{H}_5\text{O}^+\)) was one of the strongest signals in the mass spectrum of pure malonic particles measured by Q-AMS with EI energy of 70 eV and vaporizer temperature of 600 °C (Takegawa et al., 2007). That signal was also observed for MA coatings in our HR mass spectra and used as marker for MA coatings. The average background signal per aerosol particle at \(m/z\) 42 for bare \(\text{CaCO}_3\) particles was 1.4 ± 0.4 × 10\(^{-12}\) µg. The average value represented the baseline of the mass spectra at \(m/z\) 42 and the SD was derived from the noise in the mass spectra.

The coating amount for both organic compounds was derived as follows. The observed signal at the respective marker \(m/z\) was corrected for the background signal from bare \(\text{CaCO}_3\) and then scaled to the volume increase (per particle) calculated from the shift of the particle diameter \(D_p\) for the largest coating amount achieved at 80 °C coating temperature. Because of the relative large bin width compared to the growth by coating we used the \(D_p\)’s, interpolated between
the nominal size bins of the SMPS (see above). This assumed spherical core shell morphology, based on Zhao et al. (2010), where it was shown that the CaCO$_3$ particles generated by the spray-drying method were spherical. The relation between AMS-derived organic mass (baseline corrected marker signals at m/z 41 or m/z 42 particle$^{-1}$) and SMPS-derived organic mass ($\rho_{\text{org}} \times \pi/6 \times (D_p - D_{\text{PCaCO}_3})^3$) is linear within the limits of the method (see Fig. S1). For discussion we will refer to the AMS results, as we are able to detect amounts of organic coatings as small as several 10$^{-12}$µg per particle with the AMS, while these could be not be detected by the SMPS.

2.4 CCN activity measurement

The aerosol was dried to RH < 3% by another diffusion drier before the CCN activity was measured. To determine the CCN activity of the aerosol, the number concentration of the CCN of the aerosol was measured with a continuous flow CCN counter (CCNC, DMT-100, Droplet Measurement Technologies, Boulder, CO, USA). The total number concentration (CN) of the aerosol particles was synchronously measured using an ultrafine water-based condensation particle counter (UWPCP, TSI 3786; see Zhao et al., 2010). The ratio of CCN to CN (CCN/CN) is called the activated fraction ($a_f$). In cases where a polydisperse aerosol was coated, the coated aerosol particles were size selected by scanning a DMA between 10.6 and 478.3 nm, and the CCN and CN concentrations were determined for each size bin while the supersaturation (SS) kept constant (known as Scanning Mobility CCN Analysis (SMCA); Moore et al., 2010). The activated fraction was calculated after the CCN and CN concentrations were corrected for the multiple charged particles.

The activated fraction as a function of the particle size was fitted with a cumulative Gaussian distribution function (Rose et al., 2008). The turning point of the function is the critical dry diameter ($D_{\text{crit}}$ or $D_{\text{50}}$) at the set SS. The activation efficiency (i.e., the activated fraction when aerosol particles are completely activated) was 83% for the CCN instrument, determined using 150 nm (NH$_4$)$_2$SO$_4$ particles at SS = 0.85%. Besides CaCO$_3$ and coated CaCO$_3$ particles, the CCN activities of MA particles, OA particles, and mixed particles of CaCO$_3$ and MA were also measured. The MA particles were generated by spray-drying a MA solution. The OA particles were generated by heating 10.0 mL OA to 97°C in the storage bulb and then cooling the vapor to 2°C in the water cooler in a clean coating device. Then, 1.75 L min$^{-1}$ high-purity N$_2$ was used as carrying gas and went into the storage bulb through “1 N$_2$ in” entrance in Fig. 1; the “3 Aerosol in” entrance in Fig. 1 was closed. This way, pure OA particles with diameters up to 333 nm were generated. Mixed CaCO$_3$–MA particles were generated by spraying the supernatant clear solutions which were prepared by settling suspensions containing CaCO$_3$ and MA in molar ratios of about 1:1 and 3:1. The suspensions were prepared with 0.020 g MA and 0.021 g CaCO$_3$ and 0.025 g MA and 0.076 g

<table>
<thead>
<tr>
<th>OA</th>
<th>$D_p$ (nm)</th>
<th>Organic mass per particle ($10^{-12}$ µg)</th>
<th>Mole organics per particle ($10^{-20}$ mole)</th>
<th>Org. volume fraction (%)</th>
<th>$\kappa$</th>
</tr>
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<tbody>
<tr>
<td>Uncoated CaCO$_3$ 30–80°C</td>
<td>101.9</td>
<td>(backgr. m/z 41: 2.7 ± 0.9)</td>
<td>0</td>
<td>0.0</td>
<td>0.028 ± 0.0001</td>
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<td>CaCO$_3$ + OA 30°C</td>
<td>102.1</td>
<td>3.7 ± 1.9</td>
<td>1.3</td>
<td>0.8</td>
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<tr>
<td>CaCO$_3$ + OA 40°C</td>
<td>102.5</td>
<td>7.0 ± 2.8</td>
<td>2.5</td>
<td>1.4</td>
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<tr>
<td>CaCO$_3$ + OA 50°C</td>
<td>103.7</td>
<td>14 ± 3.7</td>
<td>5.1</td>
<td>2.7</td>
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<tr>
<td>CaCO$_3$ + OA 60°C</td>
<td>104.9</td>
<td>23 ± 1.2</td>
<td>8.3</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$ + OA 70°C</td>
<td>109.2</td>
<td>96 ± 3.7</td>
<td>34</td>
<td>16</td>
<td>0.0241 ± 0.0006</td>
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<td>123.7</td>
<td>390 ± 14</td>
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<td>44</td>
<td>0.0649 ± 0.0008</td>
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<table>
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<tr>
<th>MA</th>
<th>$D_p$ (nm)</th>
<th>Organic mass per particle ($10^{-12}$ µg)</th>
<th>Mole organics per particle ($10^{-20}$ mole)</th>
<th>Org. volume fraction (%)</th>
<th>$\kappa$</th>
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<tr>
<td>Uncoated CaCO$_3$ 30–80°C</td>
<td>101.9</td>
<td>(backgr. m/z 42: 1.4 ± 0.4)</td>
<td>0</td>
<td>0.0</td>
<td>0.0028 ± 0.0001</td>
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<td>CaCO$_3$ + MA 30°C</td>
<td>102.0</td>
<td>3.3 ± 0.3</td>
<td>3.2</td>
<td>0.4</td>
<td>0.0123 ± 0.0005</td>
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<tr>
<td>CaCO$_3$ + MA 40°C</td>
<td>102.1</td>
<td>6.8 ± 1.2</td>
<td>6.5</td>
<td>0.8</td>
<td>0.0231 ± 0.0008</td>
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<tr>
<td>CaCO$_3$ + MA 50°C</td>
<td>102.2</td>
<td>13 ± 1.8</td>
<td>13</td>
<td>1.5</td>
<td>0.0380 ± 0.0012</td>
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<td>CaCO$_3$ + MA 60°C</td>
<td>102.7</td>
<td>38 ± 1.6</td>
<td>36</td>
<td>4.1</td>
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<tr>
<td>CaCO$_3$ + MA 70°C</td>
<td>107.8</td>
<td>160 ± 8.1</td>
<td>160</td>
<td>15</td>
<td>0.1907 ± 0.0031</td>
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<tr>
<td>CaCO$_3$ + MA 80°C</td>
<td>121.0</td>
<td>610 ± 24</td>
<td>590</td>
<td>40</td>
<td>0.3126 ± 0.0062</td>
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CaCO$_3$ in 1000 mL Milli-Q water, respectively. The suspensions were allowed to stand for 24 h.

For aerosols where monodisperse aerosol particles with a dry diameter $D_p$ were coated, the CCN concentration was measured at different SS and the CN concentration was measured synchronously. Similarly, the activated fraction as a function of SS was fitted with a sigmoidal function. The turning point of the function is the critical supersaturation ($SS_{crit}$) and the corresponding dry diameter $D_p$ is called the critical diameter, $D_{crit}$. The hygroscopicity parameter $\kappa$ (Petters and Kreidenweis, 2007) was then calculated from the $D_p(D_{crit}−SS_{crit})$ or $SS(SS_{crit})−D_{crit}$ data set. The SS settings of the CCN counter were calibrated weekly using (NH$_4$)$_2$SO$_4$ aerosol based on the theoretic values in the literature (summarized by Rose et al., 2008).

3 Results and discussion

3.1 CCN activity of CaCO$_3$ aerosol

Before the coating experiments we determined the CCN activity of the bare CaCO$_3$ aerosol particles. It was measured by the SMCA method using polydisperse CaCO$_3$ aerosol particles. The value of the hygroscopicity parameter $\kappa$ of the CaCO$_3$ aerosol was 0.0028 ± 0.0001 derived by the least-square fitting of $D_{crit}$ as a function of $SS_{crit}$. This $\kappa$ value is quite small, indicating that the CCN activity of the CaCO$_3$ aerosol is low. Our $\kappa$ is well within the range of $\kappa$’s of 0.0011 ± 0.0004 to 0.0070 ± 0.0017 found in previous studies for wet-generated CaCO$_3$ particles (Zhao et al., 2010; Sullivan et al., 2009; Gierlus et al., 2012; Tang et al., 2016), but larger than $\kappa$ for dry-generated CaCO$_3$ aerosols (0.0008–0.0018, Sullivan et al., 2009).

The CCN activity for CaCO$_3$ aerosol passed through the blank coating device exposed to temperatures of 60 and 80°C was determined using the same method. The $\kappa$ value remained at 0.0028 ± 0.0001 up to 60°C and increased to 0.0036 ± 0.0001 at 80°C. The increase in $\kappa$ by 0.0008 at 80°C was smaller than the differences of reported $\kappa$ values for CaCO$_3$ aerosol in various studies and much smaller than the changes of $\kappa$ values measured in this study when the CaCO$_3$ aerosol particles were coated by MA or OA. So the effect of heating the CaCO$_3$ aerosol during the coating process on the CCN activity of the CaCO$_3$ aerosol was neglected. The $D_{crit}$ at different supersaturations ($SS_{crit}$) for the CaCO$_3$ aerosol and for the CaCO$_3$ aerosol passed through a blank coating device at heating temperatures of 60 and 80°C are shown in Fig. 5 (red, yellow, and green circles).

As the solubility of CaCO$_3$ in water is very low, droplet activation of CaCO$_3$ (and other mineral dust components) is often described by a water adsorption approach, wherein the solute term $B$ in the Köhler equation (Köhler, 1936; Seinfeld and Pandis, 2006; see Eqs. S1–S3 in the Supplement) is replaced by a water adsorption term. Equations (1) and (2) show application of the Frenkel–Halsey–Hill (FHH) adsorption isotherm as proposed by Sorjamaa and Laaksonen (2007) and Kumar et al. (2009):

$$B = -A_{FHH} \times \theta^{-B_{FHH}}.$$  

(1)

Therein the water coverage $\theta$ (Sorjamaa and Laaksonen, 2007) is given as

$$\theta = \frac{D_w - d_u}{2 \times 2.75 \times 10^{-4}} [\mu m].$$  

(2)

where $D_w$ and $d_u$ are the diameter of the wet particles and the insoluble core. We applied the FHH parameter for CaCO$_3$ ($A_{FHH} = 0.25$ and $B_{FHH} = 1.19$; Kumar et al., 2009) and derived a critical supersaturation of 1.52 % for CaCO$_3$ particles with $d_u = 101.9$ nm (Fig. 7, blue line). In comparison $\kappa$-Köhler theory predicts $SS_{crit} = 1.49$ % for $\kappa = 0.0028$. A $SS_{crit}$ of 1.49 % would also be achieved by $8.5 \times 10^{-20}$ mole solute per particle (Fig. 7, black line). Figure 7 also shows the $SS_{crit}$ for the bare CaCO$_3$ particles processed at 80°C temperature and the range of $SS_{crit}$ for 101.9 nm particles calculated from the range of $\kappa$’s given in the literature (Tang et al., 2016, and references therein) for wet-generated CaCO$_3$ particles.

We conclude that the surface of our CaCO$_3$ particles is a little more wettable than the dry-generated particles studied by Kumar et al. (2009). We presume formation of Ca(OH)$_2$ (HCO$_3$) structures on the surface during the spray-drying generation process as commonly observed whenever the CaCO$_3$ surface has been exposed to gaseous water or liquid water (Stipp, 1999; Stipp and Hochella, 1991; Neagle and Rochester, 1990). In case of soluble components causing the lower $SS_{crit}$, their amount must be of the order of $1 \times 10^{-19}$ mole particles$^{-1}$.

3.2 CCN activity of CaCO$_3$ particles with oleic acid coating

For the coating with OA, we selected monodisperse CaCO$_3$ aerosol particles of 101.8 nm diameter using the DMA and measured the size and chemical composition of the particles before (uncoated) and after (coated) coating with OA. The results are listed in the upper part of Table 1.

The mode diameters of number size distribution for the uncoated CaCO$_3$ particles at 30–80°C remained in the 101.8 nm size bin, identical to that selected by the DMA. Interpolation in between the size bins as described in the experimental section led to an average dry diameters of bare CaCO$_3$ of $d_u = 101.9$ nm. The mode diameters of the CaCO$_3$ particles after coating with OA in the range of 30–50°C stayed in the pre-selected size bin at 101.8 nm, which means that the layers were too thin to effectively grow the particles to the next size bin; the mode diameters increased distinctively in the temperature range of 60–80°C (Fig. 3a). However, the bin-interpolated diameters $D_p$ which are shown in
The organic volume fraction (\( V_f \)) in the aerosol particles, \( V_{OA}/V_{par} \) (\%), was calculated. Herein \( V_{par} = (V_{OA} + V_{CaCO_3}) \), where \( V_{OA} \) is the OA volume derived by AMS and \( V_{CaCO_3} \) is the volume of the bare CaCO_3 before coating (101.9 nm). \( V_{OA}/V_{par} \) for the uncoated CaCO_3 particles is by definition zero. The \( V_f \) for the coated CaCO_3 particles at 30–80 °C increased with the increase in the coating temperature from 0.8 % at 30 °C to 44 % at 80 °C (Fig. 3c, green square and Table 1). The CaCO_3 particles were indeed coated with a significant amount of OA and the amount of OA coating increased with the increase in the coating temperature. The experiments were repeated at least four times. The according SDs for the OA mass per particle in Table 1 demonstrate that the reproducibility of the experiments was good and the performance of the coating device was stable.

The activated fractions at different SS for monodisperse CaCO_3 particles with \( d_0 = 101.9 \) nm before and after OA coating at 30–80 °C are shown in Fig. 4. The top panel in Fig. 4 shows the results at 30–60 °C with up to \( 2.3 \pm 1.2 \times 10^{-12} \) µg of coating material deposited on the CaCO_3 particles (\( V_f \) up to 4.3 %). At the lowest SS of 0.17 and 0.35 %, the activated fractions were very low and independent of the presence of the coating material within the errors. When the SS increased to 0.52, 0.70, and 0.87 %, the activated fractions for the coated CaCO_3 particles were lower than those for the uncoated particles. Notably the activated fractions for the coated CaCO_3 particles decreased with the increase in the coating material in the range of \( V_f \) 0.8–2.7 %. The activated fractions for the CaCO_3 particles with different amounts of coating spread with larger SS applied. However, this trend reversed at the coating temperature of 60 °C and an OA \( V_f \) of 4.3 %, and the activated fractions at \( V_f = 4.3 \) % became higher than those at 2.7 % at the three largest SS. In summary, we found that the CCN activity of the coated CaCO_3 particles with \( V_f \) of OA in a range 0.8–4.3 % was lower than that of the uncoated CaCO_3 particles. The CCN activity of the coated CaCO_3 particles decreased with the increasing \( V_f \) in between 0.8 and 2.7 %; i.e., the CCN activity became lower when more coating material deposited on the CaCO_3 particles. This trend turned at a \( V_f \) somewhere between 2.7 and 4.3 %. As the \( D_p \) also increased at 60 °C we cannot differentiate whether the increase in the activated fractions is due to increasing size or increasing wettability.

The activated fractions of CaCO_3 particles after coating with OA with \( V_f \) of 16 and 44 % (coating temperatures of 70 and 80 °C, respectively) were considerably higher than that before coating, as shown in Fig. 4b. The increased activated fractions resulted from both the increase in particle size (Fig. 3) and the increase of the OA \( V_f \) of particles. At \( V_f \) of 16 and 44 %, the activated fractions of the CaCO_3 particles after coating increased with the increase of SS and reached complete activation. (Note that because the activation efficiency is 83 %, the activated fractions appear at values less

![Figure 3](image-url)
the sigmoidal fit (CCN activities, are higher than for bare CaCO$_3$ than 100 % at the points of full activation.) For vf of 16 and 44 % (VF = 16 and 44 %) was lower than that of the uncoated CaCO$_3$ particles. The presence of water vapor (1500 Pa) in the coating process enhances CCN activity. The increasing of residence time (23.7 s) of the coated aerosol in the flow tube had no significant effect on CCN activity in both experiments.

give κ = 0.0028 ± 0.0001 for the uncoated CaCO$_3$ particles determined by scanning the size of the polydisperse CaCO$_3$ aerosol particles as described above (see Fig. 5).

So we conclude that for vf of OA of 0.8–2.7 % the CCN activity of CaCO$_3$ particles after coating is lower than that of uncoated CaCO$_3$ particles and decreases with the fraction of OA. The trend turns at a vf of 2.7 and 4.3 %. CCN activity was higher than that of the bare CaCO$_3$ particles at vf of OA of 16 % (70°C) and 44 % (80°C) with CCN activity κ = 0.0241 ± 0.0006 and κ = 0.0649 ± 0.0008, respectively. The enhanced and reduced CCN activity of CaCO$_3$ particles coated with OA at 80 and 60°C, respectively, was also evident from the CCN activity measurement using polydisperse aerosols (Fig. 5).

A possible explanation for our observation can be based on the amphiphilic character of OA, namely that one end of the OA molecule is hydrophobic (the hydrocarbon chain), while the other is hydrophilic (the carboxyl group).

We refer to Ca(OH) (HCO$_3$) structures at the surface which offer polar surface sites to bind the hydrophilic ends (the carboxyl groups) of the OA molecules. The hydrophobic ends of OA molecules (the hydrocarbon chains) that are then exposed on the particle surface thus increase the hydrophobicity of the particle surface. Such a formation of a hydrophobic layer should be occurring until all polar sites are occupied or monolayer coverage is reached, maybe in the form of

Figure 4. Activated fractions (CCN / CN) of monodisperse CaCO$_3$ aerosol particles (d$_{50}$ = 101.9 nm) at different supersaturations before and after OA coating. With increasing coating temperatures of 30–50°C the activated fraction decreases despite the increase of organic volume fraction (vf) from 0.8 to 2.7 %. At vf of 4.3 % at 60°C this trend turns. Considering the increased particle diameter at 30–60°C and the reduced activated fraction simultaneously, the CCN activity of the coated CaCO$_3$ particles at 30–60°C was lower than that of the uncoated CaCO$_3$ particles (a). At coating vf of 16 and 44 % (T = 70–80°C) the activated fractions, and thus CCN activities, are higher than for bare CaCO$_3$ and increase with coating vf. In these two cases all particles are activated at the highest SS and SS$_{crit}$ and κ can be determined from the turning point of the sigmoidal fit (b, compare Table 1).

Figure 5. Critical dry diameters at different supersaturations (SS) of polydisperse CaCO$_3$ aerosol before (circles) and after oleic acid (OA) coating. Experiments were performed at 60°C (turbquoise diamond) and 80°C (triangles) coating temperatures. The flow tube experiments at 80°C were performed (indicated by “delayed”) at dry conditions (normal, blue triangles) and at enhanced water vapor (“wet”, brown triangles). The effect of the temperature in the coating device on the CaCO$_3$ core is negligible (red, green, and orange circles). As for the monodisperse case in Fig. 4, at 60°C coating temperature the particles are less CCN active than bare CaCO$_3$ while at 80°C the coated particles are more CCN active.
a self-assembled layer. This can hinder the uptake of water. Activation of CaCO$_3$ particles can be described by the Kelvin term and a water absorption term, e.g., FHH isotherm (Sorjamaa and Laaksonen, 2007; Kumar et al., 2009). In terms of Kelvin–FHH theory the hydrophobic OA coating will lower $A_{\text{FHH}}$ and/or likely increase $B_{\text{FHH}}$. The formation of a monolayer of OA on black carbon particles with the polar groups pointing outwards was postulated by Dalirian et al. (2017), which leads to increased activation of the black carbon particles. Thus, they observed a similar effect of layer formation, but with switched polarity.

Garland et al. (2008) suggested that OA at sub-monolayer coverage forms self-associated islands rather than uniformly covering the surfaces, and OA molecules are oriented vertically, with polar heads facing to the surface. This is in support of our working hypothesis: the formation of a hydrophobic surface film. We conclude that all hygroscopic sides on the CaCO$_3$ surface are covered at OA $\text{vf}$ somewhere between 2.7 and 4.3 %, as here the trend turns and droplet activation starts to increase again. This would place the monolayer coverage above 3 % organic volume fraction. According to the measurements and calculations of the length of OA molecule, the thickness of OA sub-monolayer on solid surfaces, and the thickness of deuterated OA monolayers at the air–water interface (Garland et al., 2008; King et al., 2009; Iwahashi et al., 2000), we estimate 2.3 nm as the likely thickness of OA monolayer on CaCO$_3$ particles; accordingly a monolayer would be achieved at about 12–13 % organic $\text{vf}$. As a consequence the re-increase of hygroscopicity starts at sub-monolayer coverage and we propose that a fraction of OA binds to already adsorbed OA tail by tail such that carboxylic groups are facing outwards.

For CaCO$_3$ particles coated with more than an OA monolayer ($\text{vf}$ = 16 and 44 % at 70 and 80 °C coating temperatures), OA in the first layer should still combine with the CaCO$_3$ surface, the heads pointing downwards. We suppose that now a portion of the carboxyl groups of the OA molecules, which are not in the first layer, will be exposed to the particle surface, similar to the formation of lipid bilayers in cells. However, We have no experimental proof for that. The particle surface then would become more hydrophilic.

When carboxylic groups of OA are exposed at the surface, the interaction of water with the OA layer becomes stronger, and the surface becomes wettable. In terms of the Kelvin–FHH approach, the surface water interaction becomes stronger and $A_{\text{FHH}}$ increases and likely also the interaction between the higher water layers ($B_{\text{FHH}}$ decreases). From this point of view water adsorption by the “OA bilayer” should become similar to thin MA layers (compare next section). In addition, when droplets form, OA will transfer to the surface of the droplets and lower the surface tension of the solution (the surface tension of OA is 0.033 J m$^{-2}$ (Chumpitaz et al., 1999), which is much lower than that of pure water of 0.072 J m$^{-2}$). Thus, the activation of OA-coated particles is probably a complex interaction between formation of a specific hydrophobic layers and more hydrophilic multilayers, surface tension effects, and, for the largest coating amounts, simple size effects. As shown in Fig. 7, $SS_{\text{crit}}$ for OA is lower than for thin MA coatings, probably because of the surface tension effect, but higher than for thick MA coatings, because of the missing solute effect.

The CCN activity of all oleic-coated particles is higher than the CCN activity of pure OA. Our CCN activity measurement showed that pure OA particles up to 333 nm did not activate at 0.87 % SS; this sets an upper limit for CCN activity of OA particles ($\kappa < 0.0005$), in agreement with Kumar et al. (2003) and Broekhuizen et al. (2004). In liquid state OA forms micelle-like structures; the hydrophilic ends (the carboxyl groups) of OA molecules tend to combine together by hydrogen bonds and the hydrophobic tails (the hydrocarbon chains) are exposed at the outside (Iwahashi et al., 2000; Garland et al., 2008). The arrangement of OA molecules in pure OA particles should be similar. Hydrophobic tails facing outwards can explain the hydrophobicity of the particle surface and the hindrance of the uptake of water, making the CCN activity of pure OA particles very low. For sub-monolayer coatings of OA of $\text{vf}$ 0.8–2.7 % the CCN activity seems to approach that of pure OA. However, the arrangement of OA molecules in these thin coatings will be influenced by the CaCO$_3$ core with its polar, hydrophilic sides differing from pure OA particles and can thus be less hydrophobic.

Even at the largest coating with an organic $\text{vf}$ of 44 %, the coating thickness is about 10 nm, which corresponds to about only four monolayers of OA (assuming the thickness of OA monolayer on CaCO$_3$ particles is about 2.3 nm). Additionally, the arrangement of OA molecules will still be likely influenced by the CaCO$_3$ core. Water can probably adsorb at the carboxylic groups facing outward (“bilayer” type structure) and diffuse through the thin OA coatings. It may form an adsorbed water phase near the CaCO$_3$ surface. This could push the OA out to act as surfactant which lowers the Kelvin term. Such processes should also happen in pure OA particles. Because of the presence of CaCO$_3$ core the SS to achieve this is lower than for pure OA.

The phenomenon described above is reported for the first time in the studies on the CCN activity of multicomponent aerosols. This phenomenon also shows a limitation of the otherwise very useful mixing rule (Petters and Kreidenweis, 2007) for multicomponent aerosols with specific morphologies.

In Fig. 5 we additionally show the influence of water vapor on CCN activity of CaCO$_3$ particles coated with OA for the highest coating temperature (80 °C) and thus largest OA amount. Herein we determined $SS_{\text{crit}}$ at different supersaturations ($SS_{\text{crit}}$) for polydisperse CaCO$_3$ aerosol particles (by SMCA). The experiments were performed at RH 0.3 % and at RH 3 % at the coating temperature of 80 °C on cooling to RT the RH increased to 47 %. The presence of more water vapor (1500 Pa) in the coating process increased $\kappa$ somewhat and enhanced the CCN activity. This is of importance since
RH will often be larger than 0.3 % when coating appears in the atmosphere. This will be discussed further in context of MA coatings at enhanced water vapor.

3.3 CCN activity of CaCO$_3$ particles with malonic acid coating

For the study with MA coatings, the CaCO$_3$ particles were also size selected with a diameter of 101.8 nm. The size $D_p$ and chemical composition of CaCO$_3$ aerosol particles are listed in Table 1 before and after coating with MA at temperatures in a range of 30–80 °C. The mode diameter did not shift after coating in a temperature range of 30–60 °C, but it increased for coatings at 70 and 80 °C with increasing coating temperature. The size bin interpolated particle diameter $D_p$ of the MA-coated particles increased monotonically with the coating temperature. The average of the interpolated diameter of bare CaCO$_3$ particles in the temperature range 30–80 °C was $d_u = 101.9$ nm.

Values of the MA marker $m/z$ 42 per particle were significantly larger for CaCO$_3$ particles after coating at 30–80 °C and the MA mass increased from $3.3 \times 10^{-12}$ to $610 \times 10^{-12}$ µg per particle with the coating temperature (Table 1, Fig. 3c). The organic $v_f$ of MA ($V_{MA}/(V_{MA} + V_{CaCO_3}$, %) was calculated as in the case of the OA and ranged from 0.4 to 40 %. As for OA, the MA experiments were repeated at least four times and the reproducibility and stability were good (see SDs in Table 1).

The activated fractions at different SS for 101.9 nm CaCO$_3$ particles before and after coating with MA at 30–80 °C are shown in Fig. 6. SS$_{crit}$ was determined by fitting a sigmoidal function to the data and the $\kappa$ value was calculated from the $D_p$ ($D_{crit}$) and the corresponding SS$_{crit}$. The results are listed in Table 1. In this procedure we had to neglect the contribution of double-charged particles because the step in the CN/CCN vs. SS data in Fig. 6 is not sufficiently expressed to separate a plateau for multiply charged particles (e.g., Sullivan et al., 2009). The exception is the MA coating with $v_f = 0.4 \%$. For this case we compared a sigmoidal fitting both from the beginning (the first point) and from the multiply charged plateau (the third point) to the “completely activated plateau” (Fig. S3). We yield SS$_{crit} = 0.887 \pm 0.005 \%$ for fitting from the beginning and SS$_{crit} = 0.900 \pm 0.013 \%$ for fitting from the multiply charged plateau, which is a difference of 0.013 %. The underestimate in SS$_{crit}$ is the largest (0.013 %) when the MA mass is the smallest ($v_f = 0.4 \%$) and the underestimate will be reduced with increasing $v_f$ of MA. At the largest two MA $v_f$ it can be neglected. We have to concede a systematic error in SS$_{crit}$, but it is distinctively less than 0.02 %.

The $\kappa$ values of the CaCO$_3$ particles after coating with MA at 30–80 °C were higher than the $\kappa$ value of the uncoated CaCO$_3$ particles ($\kappa = 0.0028 \pm 0.0001$) and increased with the increasing coating MA mass per particle and increasing MA $v_f$. The CCN activity of the CaCO$_3$ particles increased monotonically after coating with increasing MA mass. This result differs from that of OA, which is not surprising since MA is easily soluble in water.

The $\kappa$ value for the CaCO$_3$ particles after coating with a mass of MA as small as $3.3 \times 10^{-12}$ µg per particle and $v_f$ of MA of only 0.4 % was 0.0123 ± 0.0005, thus considerably larger than the $\kappa$ value for the uncoated CaCO$_3$ particles ($\kappa = 0.0028 \pm 0.0001$). This suggests already that a small amount of MA can significantly enhance the CCN activity of CaCO$_3$ particles. The phenomenon that traces of watersoluble substances can strongly affect droplet activation has been reported before (Bilde and Svenningsson, 2004).

We applied Koehler theory to CaCO$_3$ particles coated with MA, assuming that the MA coating will fully dissolve in water when droplets form (see Eqs. S1–S3 in the Supplement). Increasing MA solute decreases the activity of water in solution and lowers the critical supersaturation SS$_{crit}$ for droplet activation.

The resulting Koehler curves, i.e., equilibrium SS over the solution droplet as a function of the wet diameter $D_w$, are shown in Fig. S2. Therein the maximum of each SS curve is the critical supersaturation (theory SS$_{crit}$). In Table S1 and Fig. 7 we compare the SS$_{crit}$ predicted by the Köhler approach (red) with the observed SS$_{crit}$ (black). Koehler theory overpredicts SS$_{crit}$ for thin coatings substantially, meaning it underestimates the hygroscopicity of the thinly coated particles. But with increasing coating Koehler theory approaches the observed SS$_{crit}$ and SS$_{crit}$ for a particle of 121 nm diameter composed of pure MA (red circle).

From the Koehler results we derived the water content of the particles at SS$_{crit}$ and we calculated modalinity and mass fraction of the solute in the solution at the point of activation. The modality at minimum and maximum MA load of
ter agreement and still allow for smaller van’t Hoff factors (Varga et al., 2007). As an example, a surface tension of 55 % of \( \sigma_w \) and a van’t Hoff factor of 1 will bring \( S_{S\text{crit}} \) predicted by Koehler theory and observation in agreement for the thinnest coating. However, a surface tension of 55 % of \( \sigma_w \) will cause disagreement for the thickest coating, because the solute term gains in importance. The findings for the mixed solutions of MA and water-soluble ammonium sulfate are likely not directly transferable to our systems with insoluble inorganic core, where we expect dilute aqueous solutions of 0.006 mol kg\(^{-1} \) of MA at the activation point. At such concentrations MA does not reduce \( \sigma_w \); moreover, in the study of Ruehl et al. (2016) MA was one of the more Koehler \( \kappa \) behaving organics.

In Fig. 7 we show the prediction of \( S_{S\text{crit}} = 1.52 \% \) for activating CaCO\(_3\) by the Kelvin–FHH theory with the CaCO\(_3\) parameters taken from Kumar et al. (2009). \( S_{S\text{crit}} \) for our bare CaCO\(_3\) particles is 1.49 % and the lower \( S_{S\text{crit}} \) should be due to a more adsorptive surface, e.g., the presence of Ca(OH)(HCO\(_3\)) structures. According to classical Koehler theory the equivalent of 8.5 \times 10\(^{-20} \) moles of dissolvable entities would be needed to explain a \( \kappa \) of 0.0028 and \( S_{S\text{crit}} \) of 1.49 %, which is only about one-quarter of the moles MA in the thinnest MA coating. Therefore, whatever makes our CaCO\(_3\) particles wettable is not sufficient to explain the low \( S_{S\text{crit}} \) of 0.9 % at the thinnest MA coating in terms of Koehler theory.

We estimate monolayer coverage by MA at 2–3 % \( \nu \); this would be achieved in between MA mass loads of 13 \times 10\(^{-12} \) and 38 \times 10\(^{-12} \) \( \mu \)g per particle. Thus a sub-monolayer coating of 3.3 \times 10\(^{-12} \) \( \mu \)g MA per particle caused a drop of \( S_{S\text{crit}} \) from 1.49 to 0.9 and increased \( \kappa \) from 0.0028 to 0.012. Therefore we conclude that CaCO\(_3\)–MA coatings show a non-Koehler behavior at thin coatings, but approach Koehler behavior with increasing MA load.

This means there must be specific interactions between MA and the CaCO\(_3\) surface which eases water adsorption and CCN activation. We refer to the Ca(OH)(HCO\(_3\)) structures that likely exist on the particle surface. When CaCO\(_3\) particles are coated by MA (or OA) the hydrophilic sides can serve as polar surface active sites for accommodation of the acids. In the case of MA there is no long hydrophobic organic chain, but there is a second carboxylic group which could still support the adsorption of water films.

In terms of Kelvin–FHH theory one could explain the observed low \( S_{S\text{crit}} \) for thin MA coatings by net stronger interaction with water (higher \( A_{FHH} \)) and/or stronger interaction between the adsorbed water layers (lower \( B_{FHH} \)) compared to bare CaCO\(_3\). If coatings become thicker the Koehler solute effect starts increasingly to contribute and eventually controls the CCN activation. Our data are not sufficient to determine \( A_{FHH} \) and \( B_{FHH} \). (The only system in the literature which comes close – in a far sense – is calcium oxalate monohydrate, with \( A_{FHH} = 0.57 \) of and \( B_{FHH} = 0.88 \) (Kumar et al., 2009). Using these FHH parameters will lead
to $SS_{\text{crit}} = 0.53\%$, comparable with our observed value of $0.56\%$ for $13 \times 10^{-12}\ \mu\text{g}$ MA coating, which represents an organic vf of 1.5% and thus is close to monolayer.)

$D_{\text{crit}}$ at different supersaturations ($SS_{\text{crit}}$) for polydisperse CaCO$_3$ aerosol particles before and after coating with MA is shown in Fig. 8. Our observation of $\kappa = 0.25 \pm 0.04$ for pure malonic acid is consistent with the $\kappa$ derived from the data of Kumar et al. (2003) ($\kappa = 0.20–0.25$) and Prenni et al. (2001) ($\kappa = 0.24$), but significantly lower than the $\kappa$ derived from the data of Giebl et al. (2002) ($\kappa = 0.41–1.04$). The behavior of polydisperse coated aerosol was similar to the result obtained from the monodisperse CaCO$_3$ aerosol particles.

In Fig. 8 we added results for coating in presence of enhanced water vapor (1500 Pa) and aerosols generated by spraying mixtures of MA and CaCO$_3$. At the coating temperature of 60°C, when the RH increased from 0.7 to 7% and eventually to 47% at RT, the CCN activity of the coated CaCO$_3$ particles increased substantially (compare “dry” (green triangles) and “wet” (lilac triangles) in Fig. 8). The effect is more distinct than for the OA coating shown in Fig. 5, and $\kappa$ increases by about an order of magnitude. In wet conditions, the reaction between CaCO$_3$ and MA may be more efficient and formation of calcium malonate will reduce $d_{\text{ins}}$, i.e., the diameter of the insoluble core; according to Eq. (S1) this may be the reason for the higher CCN activity at the higher RH. The hypothesis of malonate formation is supported by the CCN activity of “calcium malonate” aerosols, generated by spraying solutions containing CaCO$_3$ and MA with molar ratios of about 1 : 1 and 3 : 1. Here the CCN activity is similar to that arising in the coating process in the presence of water vapor. The change of the Ca/malonate ratio from 3 : 1 to 1 : 1 had no large effects. But, taking the data of pure MA particles also into account, there is a trend to lower $\kappa$ with increasing Ca in the initial solution.

The increase of residence time (by 23.7 s) had no significant impact on CCN activity for both OA coating and MA coating at both dry and enhanced water vapor conditions, probably because the coating process was already completed in the coating device and no further reactions occurred in the flow tube.

Our findings may be important for aging processes of mineral particles in the atmosphere. The dependence of CCN activity of the coated particles on RH during the coating process will help to enhance the increase of the CCN activity by the coating process as water will be abundant in many instances. The effect probably will be relatively small for OA and similar organics, which are hardly water-soluble, but strong for MA and similar organic acids, which are highly water-soluble.

4 Conclusions

The CCN activity of CaCO$_3$ particles with oleic acid and malonic acid coatings was investigated in this study. The results show that oleic acid coating and malonic acid coating have different impacts on the CCN activity of CaCO$_3$ particles. This can be attributed to the amphiphilic property of oleic acid in contrast to the high water solubility of malonic acid. Small amounts of oleic acid coating (vf $\leq 4.3\%$) decreased the CCN activity of the CaCO$_3$ particles, while more oleic acid coating (vf $\geq 16\%$) increased it. This phenomenon was reported here for the first time and was attributed to stepwise passivation of the active sites of CaCO$_3$ by oleic acid. Once all active sites are occupied we suggest the formation of a lipid-like bilayer with the carboxylic groups facing outwards.

In contrast, malonic acid coating (0.4–40%) increased the CCN activity of CaCO$_3$ particles regardless of the amount of the coating. The CCN activity of CaCO$_3$ particles with malonic acid coating increased with the amount of the coating. Even a small amount of malonic acid coating (vf $\geq 0.4\%$) significantly enhanced the CCN activity of CaCO$_3$ particles from $\kappa = 0.0028 \pm 0.0001$ to $\kappa = 0.0123 \pm 0.0005$. Increasing the RH during the coating increased the CCN activity of the CaCO$_3$ particles with malonic acid coating, probably because more CaCO$_3$ reacted with malonic acid to soluble calcium malonate. This process will help to increase the CCN activity.

Figure 8. Critical dry diameters at different supersaturations (SS) of polydisperse CaCO$_3$ aerosol before (circles) and after malonic acid coating (triangles). Experiments were performed at 60 and 80°C coating temperatures. The results are similar to the monodisperse case in Fig. 6. Critical dry diameters as a function of SS are also shown for malonic acid particles and particles that were generated by spraying mixed solution with molar ratios of CaCO$_3$/malonic acid of 1 : 1 and 3 : 1. The CCN activity decreases with increasing CaCO$_3$ content. The flow tube experiments at 60°C were performed (indicated by “delayed”) at dry condition (blue triangles) and in presence of 1500 Pa water vapor (magenta triangles). The presence of water in the coating process substantially enhanced $\kappa$ and CCN activity. The increasing of residence time (23.7 s) of the coated aerosol in the flow tube had no significant effect on CCN activity in both experiments.

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Although malonic acid is soluble in water, SS$_{\text{crit}}$ for MA-coated particles was overpredicted by Köhler theory. Our results indicate that thin MA coatings provide a wettable particle surface, which favors adsorption of water. For thicker coatings the coated particles approached Köhler behavior because of increasing importance of the solute effect.

Mineral aerosol is one of the most abundant components of the atmospheric aerosol, but its low water solubility limits its CCN activity. This study showed that water-soluble organic acid coating might significantly enhance the CCN activity of mineral aerosol particles. This could lead to mineral aerosol playing a more important role in cloud formation.

Data availability. Access to data can be requested from the corresponding authors.

The Supplement related to this article is available online at https://doi.org/10.5194/acp-18-7345-2018-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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