Review for a manuscript titled: Ice nucleation activities of soot particles internally mixed with sulphuric acid at cirrus cloud conditions, by Gao et al., 2021, ACPD

Gao et al. present laboratory experiments where they tested the ice nucleation activity of soot particles. Propane combustion particles were generated in a controlled laboratory setup using a burner. In addition a commercial soot sample was used. The ice nucleation activity was tested with a HINC chamber, operated at fixed temperature steps between -55 C and -30 C while performing *RH*-scans at each temperature step. These conditions are relevant for ice formation in cirrus and mixed-phase clouds. The ice nucleation activity is tested for bare soot particles and compared to the ice nucleation activity of soot with varying degrees of H2SO4 coating. The ice nucleation experiments are supported by a suite of auxiliary measurements to characterize the chemical and physical properties of the soot particles and the impact of coating thickness on these properties. The authors explain their observation using the pore condensation and freezing mechanism, its inhibition and enhancement with respect to coating. The authors then present a hypothesis of a 3 step coating process.

Overall, the authors find the tested combustion soot particles to be worse ice nucleation particles in comparison to the commercial soot and demonstrate how coating thickness can affect some of these properties.

The presented study results fall within the scope of Atmospheric Chemistry and Physics (ACP) journal. The observations in this study are largely in-line with previous work and further help to understand the role of soot in cloud formation processes. The manuscript is clearly written however, the conclusions drawn are not sufficiently supported by evidence and some ambiguity remains. These issues need further clarifications. Below, I list my comments and suggestions that should be addressed upon revising the manuscript.

Major comments:

The study is well structured and has the suitable experimental design to conduct ice nucleation measurements. However, the study lacks novelty, with some portions of the study being a repetition of previous experiments with the same chamber or in other institutes e.g. L349,L429, L522.

The results, as is, have high degree of uncertainty. Discrepancies between EDX, optical sizes, mobility sizes and electron microscopy sizing on grids and equivalent ML are mentioned but waived aside without a deeper discussion on the uncertainties of the study. Lack of statistical analysis presentation, in particular in electron microscopy, create high ambiguity for the derived conclusions. Some of the uncertainties, like chemical reactions, are mentioned e.g. L581 but not sufficiently discussed while some are not mentioned at all. The authors mention the presence of the doubly charged particles however, it’s not clear which sizes are playing the main role in the nucleation process. Since size is a key factor both for coagulation, condensation and ice nucleation, this aspect of the study should be clarified. A deeper discussion on the physicochemical properties of H2SO4 to the same extent as water freezing is absent.

Minor, specific and technical comments:

L1: ‘Activities’ replace with activity. Also I’d recommend to amend the title to include the bare soot measurements and to clarify that these are laboratory experiments. Also see comment L625.

L10: There is a problem with this sentence, if they are only candidates, what makes them so important? Perhaps use potential instead of important.

L10: comma after formation

L14: I think a sentence of justification is missing here for the choice of propane flame soot or a commercial BC. e.g. “Generic BC surrogates are often used in laboratory experiments. In this study….”

L16: activities - in line 13 you say ability, but study activity? Please keep consistency or explain the differences throughout the text between ability and activity.

L25: abilities – same comment

L35: please add https://doi.org/10.1029/2021JD034649 to Liu et al., 2020.

L36: The numbers cited here are from a review by Bond et al. published 8 years ago and data collected more than a decade ago. Please see if there are additional newer reports. Otherwise, short-lived climate forcers suggest a continuous decline in carbonaceous emissions. Moreover, there is a lack of accurate global quantification of this short lived element (IPCC AR6 report, Chapter 6). These caveats should be mentioned.

L38: aircraft plural is still aircraft

L65: “…vigorous convection” – reference missing.

L69: abilities – see comment for L16 and throughout the manuscript

L72: "potentially… potential”, I suggest to reword. For example: Thus, it is possible that the mixing state of soot particle with H2SO4 coating may regulate its INP activity.

L75: remove abilities, remove in-situ

L75: some references could be useful here e.g. Brown et al. DOI: 10.2514/6.2018-3188

L76: please include some references for lab studies of aviation soot.

L77: “contrail dissipation” – please add reference

L77: stick with one form ‘in-situ’ like in line 75 or ‘in situ’.

L88: in line 85 you talk about aviation soot particle surrogates then here you mention graphite, It is not clear how graphite is a surrogate of aviation soot and how this is relevant here.

L90: Mahrt et al. 2018 – please replace with Marcolli C. 2014 and others. I believe it was suggested also much earlier by others.

Marcolli, C.: Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities, Atmos. Chem. Phys., 14, 2071-2104, 2014.

L116: I'd remove the text after wettability and refrain from mentioning contact angle in the manuscript for two main reasons: First and foremost, you don’t report or use contact angle measurements in this study. Secondly, the concept of contact angle measurements and inference to nano-scale dynamic processes is questionable to the least. No surface energy component calculations are truly quantitative nor are they necessarily based upon universally accepted theoretical considerations (see Marmur et al. 2017;Marmur 2006; Strobel&Lyons 2011). Most theories of solid surface energy have a basis in Young's equation, which employs the equilibrium contact angle. In surface energy calculations, many in the surface science field tend to use the so-called static contact angle, which we now know to be meaningless (Marmur et al. 2017), or else the advancing angle, assuming that one of these angles is the equilibrium angle or at least very close to the equilibrium angle. However, the equilibrium contact angle cannot be determined on practical BC surfaces.

Contact angle is indeed a parameter that can reflect surface functionality however it was and continues to be a highly biased method for getting absolute characterization of the surface. If experimentally measured, it is often highly dependent on the methodology of the measurement. Hoose and Mohler (2012) suggested to use a probability distribution function for contact angle. Marcolli (2016) when using contact angle ignored the correction for the size dependence of surface tension and assumed a zero contact angle, she also mentioned that “accurate values for the contact angles between water and the pore walls of our investigated particles are not available”.

Marmur, Abraham, Claudio Della Volpe, Stefano Siboni, Alidad Amirfazli, and Jaroslaw W. Drelich. "Contact angles and wettability: towards common and accurate terminology." Surface Innovations 5, no. 1 (2017): 3-8.

Marmur, A.: Soft contact: measurement and interpretation of contact angles, Soft Matter, 2(1), 12–17, doi:10.1039/B514811C, 2006.

Strobel, M. and Lyons, C. S. (2011), An Essay on Contact Angle Measurements. Plasma Processes Polym., 8: 8-13. doi:10.1002/ppap.201000041

Marcolli, C. (2016), 'Pre-activation of aeosol particles by pore condensation and freezing', Atmos. Chem. Phys., 2016, 1-48.

Hoose, C, and O Möhler. "Heterogeneous Ice Nucleation on Atmospheric Aerosols: A Review of Results from Laboratory Experiments." Atmospheric Chemistry and Physics 12, no. 20 (2012): 9817-54.

L127: replace ‘need’ with ‘could benefit from’

L134: in the abstract you also mention mixed-phase, but the conclusions are only about ice nucleation in cirrus clouds?

L137: The samples are not ‘experimental’ perhaps ‘test samples’?

L142: Switch places between the name and the HINC acronym like you did in line146 for DMA

L143: part of the exhaust air

L148: mobility diameter – change throughout the manuscript.

L164: remove ‘Experimental’

L166: mention it's a diameter in this sentence.

L167: The aerosol sample – does it contain only the soot aerosol? Are there byproducts in the propane combustion process e.g. gases/vapors? If there are any, where do they go, do they follow the aerosol coating and IN path? Would this direct injection affect your measurements?

L168: home change to in-house

L174: CPMA - see comment L142

L175: sucked changed to pulled

L176: microscopic grids change to microscopy grids

L177: Rephrase. Not clear distinction from what? Other studies in this field? Your previous studies?

Is the “generation of coated soot...and the real time analysis of their properties...” are the only novelty components of this study? why is it important to mention this distinction? Also see my major comment on the significance/novelty of this study.

L178: not sure what online means here? Real-time?

L179: see comment in L16.

L186: finally change to consequently

L191: LabVIEW

L207: indicating no pure nucleated H_2SO_4 - add reference to subsection where these results are presented.

L211: becomes absent - what does that mean? There is no longer homogeneous nucleation or the mode moves below your detection threshold or rate of coagulation is higher than homogeneous nucleation?

L211: decreases dramatically - please elaborate, is it the difference between nucleation and coagulation rates? What portion coagulated and how much condensed? have you tracked the temperature in this coating process? how mixing the flows with different temperature affects the evaporation rate of H_2SO_4? could it affect the repeatability?

L215: we are confident change to we conclude

L220: a known changed to defined?

L252: ‘and’ change to ‘so that’

L258: what’s the reasoning for using a water CPC? would you expect differences in comparison to butanol CPC for coated and bare soot counting?

L260: see comment L148

L262: remove mathematical

L262: see comment L148

L266: remove ‘by the’

L274: see comment L148

L289: What is the reasoning for bringing this issue up here if there is no solution provided? Stating that it provides still relatively comparable information doesn’t resolve the issue. This should be moved into discussions of uncertainties in the study. What type of BET was used for the specific surface area of your samples?

L292: Whereas 400 nm size selected soot particle does not show apparent size growth – why?

L302: home – change to in-house

L331: see comment in L16.

L338: what aerosol is used to calibrate the 780nm diode in the OPC? In appendix C, have you evaluated the response of the OPC to different soot types and diameters directly without passing through the chamber? Is it possible that the OPC mis-sizes non spherical, light absorbing soot with higher refractive index with a complex component?

The coated soot is often studied for its enhanced light absorption and other optical property changes, would that affect the OPC sizing? Bhandari et al. 2019 wrote that compaction affects the soot optical properties. Light absorption and scattering change when a soot particle undergoes morphological transformations.

The recommended operating temperature of the OPC by the manufacturer is 0º C to +50º C, what are the expected biases in detection and sizing for air/aerosol flows at low temperature, down to -55? Would you expect humidity condensation on OPC windows?

L360: see comment L116. You can cite here the earlier studies. It can be attributed to wettability but not necessarily contact angle.

L360: There is no mention of the solvents/organic content pre-existing in FW200 as indicated by the manufacturer. Volatile content gas chromotography or DTA-TGA analysis could shed some light on the chemistry or its wt%. Without it, some discussion is needed about the possible properties of this content and whether glass transition of those organic compounds could impact the IN activity in these temperatures.

L409: Is there a possibility of homogeneous nucleation of the acid and coagulation with soot, Coagulation is strongly affected by residence time. would that be possible on these time scales?

L413: T – spell out temperature throughout the manuscript

L413: inhibits – change to ‘could be the main cause for inhibition of the’

L414: see comment L413.

L414: From – change to ‘In’

L415: shows coherence- change to ‘is coherent’

L429: see comment L413

L430: see comment L413

L440: more uniformly - doesn’t that contradict what you wrote in L405?

L455: see comment L116. I think this proves further that the contact angle measurement is not the best choice of technique to include in such studies.

L460: see comment L413.

L461-462: not clear who you are citing here Koehler 2009 or Henson 2007?

L463: doesn’t that contradict L440?

L478: soot aggregate - how do you define an aggregate here? is it a single aggregate of spherules, please elaborate. Is it consistent with definitions by Long et al. 2013?

Long, C. M., Nascarella, M. A., and Valberg, P. A.: Carbon black vs. black carbon and other airborne materials containing elemental carbon: Physical and chemical distinctions, Environ. Pollut., 181, 271–286, https://doi.org/10.1016/j.envpol.2013.06.009, 2013

L480: see comment in L148. Small particles with a small mobility size contain less pore volume - Is this generalization of mobility diameter accurate? doesnt that depend also on spherule size? Did you mean ‘Small FW200 soot particles’?

L489: In this interpretation of observation, I couldn’t find a discussion about the effect of cooling rate, and hydration of the sulfuric acid on its glass transition and changes around the glass transition range, see Zobrist et al 2008; Williams & Long 1995 and others. Also see my last Major comment.

Zobrist, B., Marcolli, C., Pedernera, D. A., and Koop, T.: Do atmospheric aerosols form glasses?, Atmos. Chem. Phys., 8, 5221–5244, https://doi.org/10.5194/acp-8-5221-2008, 2008.

Williams, Leah R., and Forrest S. Long. "Viscosity of supercooled sulfuric acid solutions." The Journal of Physical Chemistry 99.11 (1995): 3748-3751.

L506: sentence too long.

L506: remove ‘measurement results’

L506: remove ‘characterization results’

L516-519: is that the "collapse" you described in L293? it sounds less obvious here.

L522: fractal dimension - have you explained what this is or how 1.86 was calculated?

L524: coating does not result in a significant soot surface topography change – it doesn’t look like there is any morphological difference between 8d,e,f except the addition of a large amount of acid. No evidence to indicate a collapse mentioned in L293 and shown in Fig. 3c.

L529: resulted from the impaction of soot-aggregates on the Cu grid - how do you know that? Further in the text, you’ve discussed possible other biases of sample transfer, of measurement with SEM in vacuum. Also, how would electron beam interaction with nonconductive particles affect the sample and imaging?

L531: could you also describe what this figure shows in C2a,C2b, C2c?

L542: Small aggregates can also coagulate while transporting in the aerosol flow - coagulation is highly dependent on residence time, if you suggest coagulation is possible, what about coagulation between soot and small droplets of sulfuric acid below your detection range or those that are neutral in charge?

Also do you see this same extent of coagulation with thinly or thickly coated?

L547: why did you decide to show this aggregate? is that a typical image?

L551: some extent aggregate compaction - previously I believe you called it collapse? Consider toning down the previous description.

L554: the shrinkage, collapse, and compaction terminology should be consistent throughout the text. Could you explain the differences between the percentage of decrease in diameter in Fig 3a, and the shrinkage observed in Fig. 8c?

L559: a supplementary video recording starting with the initial state could provide valuable qualitative information about the structure for the readers.

L569: demonstrated that

L569: shows – change to has

L570: 'to indicate' – change to 'to characterize the'

L571: S – spell out sulfur and all the other elements throughout the text

L576: see comment L571

L580: S,O see comment L571

L581: This may suggest that there is a reaction between mCASTblack soot and H2SO4 depleting some O content in the process - If you are suggestion that there is a chemical reaction taking place, wouldn't that have an impact on IN activity? On partial vapour pressure? This is in addition to the changes in H2SO4 viscosity (see comment L489). These processes, which are barely discussed may affect your hypothesis. See Major comments.

L584: see comment L571

L586: Does that contradict your interpretation of observations in L529? Is it possible that evaporation of coating would induce morphological changes like compaction, similar to droplet evaporation in cloud processes? See also comment to Fig.12.

L590: be H2SO4 droplets – Fig. 11a? not clear where it's shown.

L596: would be good to attach a datasheet with all the known properties of FW200 provided by the manufacturer as a supplement. The product may be discontinued in the future and the information from the manufacturer will be lost.

L596: If all the reservations in this paragraph are true, it is not clear how the statement in L614 (robust evidence) is supported. Or how EDX analysis can be used at all to explain any coating observations in this study.

L610: Firstly, this is not unequivocally evident from your analysis. Secondly, there could be other possible interpretations that you haven't discussed, see comment L489. I suggest to tone down these statements.

L625: This section should be revised or even removed. The title/focus of the manuscript is ice nucleation. Is the hypothesis brought up here is highly relevant to the main topic? Perhaps the title should be changed.

L645: The fatty acid example is irrelevant to the hypothesis of sulfuric acid coating process. What these two have in common?

L652: Im not sure I understand the physics of this process, could you elaborate further? See comment to Fig.12.

L654: please avoid drama in science, "supported by the compaction of thickly coated..."

L658: remove a dramatic

L663: robust support from measurements in this study – I'd highly recommend to tone down the statement and properly address the major comments.

L674: the sentence here is fairly general and doesn't require citation, unless you want to refer the readers e.g. 'see examples in Kanji et al 2017'?

L678: morphological properties and size?

L688-L697: wouldn't it also depend on the dynamic expansion pulse into the low pressure environment at high altitude and induced supersaturation?

L699: similar to our – change to similar to the FW200 soot sample used here

L705: it is likely that ice crystals can be induced by them – reword.

L712: loses change to loose

L719: carbon poor?

L774: because a 200 nm pure H2SO4 particle has a mass of 7.7 fg - what about the bottom edge of the PSD for pure H2SO4?

L805: to be reliably detected in the 5 µm channel - Korhonen et al 2021 selected 6 micron as their bottom threshold. Would lamina flow peripheral regions have slightly different RH conditions?

Korhonen, K., Kristensen, T. B., Falk, J., Malmborg, V. B., Eriksson, A., Gren, L., Novakovic, M., Shamun, S., Karjalainen, P., Markkula, L., Pagels, J., Svenningsson, B., Tunér, M., Komppula, M., Laaksonen, A., and Virtanen, A.: Particle emissions from a modern heavy-duty diesel engine as ice-nuclei in immersion freezing mode: an experimental study on fossil and renewable fuels, Atmos. Chem. Phys. Discuss. [preprint], https://doi.org/10.5194/acp-2021-111, in review, 2021.

L867: believed - In my opinion EDX is not a suitable technique to analyze organics, it is more suited for the analysis of inorganic materials, rather than materials that contain for the most part all the same organic elements bonded differently. Especially in the case of a commercial FW200.

L868: impaction/drying - you also mentioned earlier the electron beam evaporated the acid.

L872: particle concentration is high - why this was not addressed during the experiments? This is a known issue, which is controlled by grid size selection, collection time, and flow settings.

L874: a high probability - I believe the collection efficiency is something that can be calculated. See previous comment. Was the ZEMI instrument calibrated for proper collection in previous studies?

L877: 3000 cm-3 - what is the highest number of particles the instrument can size without coincidence bias that will cause mis-sizing?

L881: ‘suggesting’ - see comments L338, L877.

A better way would be to analyze the volatile components while heating the collected particles, or analyzing the exhaust of a thermal denuder.

L908: primary particle edges are more ambiguous in Fig. C4f for thickly coated soot particles - this is not obvious, a higher magnification is shown in C4f. what differences one would expect to see for organic volatile content in ultra-high vacuum for HRTEM and high energy beams?

Figures like this of lower significance and their description can be moved to a supplement.

L921: see comment in L867. I think figures C4-C11 can be moved to a supplement. A more informative figure/table would be of a statistical analysis for these measurements, which is the standard practice in electron microscopy for extrapolation of properties to a broader sample area.

L921: the areas of interest

L976: is this a thesis? please indicate.

L1068 and others: The DOI links dont work. All those should be changed to the right format e.g. https://doi.org/10.5194/acp-17-15199-2017.

L1994: 2020b should be listed after 2020a?

Fig. 1: Exhaust filter, flow splitter – correct labels,

1.5 L/min does that belong to the CPMA on the right?

Fig. 2: remove the turquoise box in the CPC, irrelevant

Table 1: first column coating T – change to H_2SO_4 evaporation T

Fig. 3: The different soot types should be indicated on the plots too.

caption: size – change to diameter measured by SMPS.

Effective – change to calculated effective

Table 2: first column, please elaborate what is that temperature. Also, is this table really necessary or the numbers can be mentioned in the main text?

What’s the significance of mentioning 30C results, which suggest, if I understood correctly, that there might be no coating?

Fig. 10: I suspect multiple measurements were done to make this figure rather than one single measurement for each nanoparticle type and inference for the whole grid. Please include some statistical analysis of sampling in different locations on same particle and/or on different particles on the grid in each category and add stdev values to elemental percentage that you present. With the currently presented values, the difference significance between all 3 is not obvious.

why did you choose to use a precision of 1 decimal for carbon and oxygen but 2 decimals for sulfur?

Fig. 11: see comment for Fig. 10.

Fig. 12: interestingly, you illustrate here the sulfuric acid as homogeneously nucleated droplets rather than vapour condensing in monolayers? Or perhaps I got it wrong?

I'm not sure I understand this conceptual collapse in Fig. 12d. what forces are causing it? I would expect the particle to collapse upon drying due to surface tension exerted on the aggregate rather than during the coating process.

Also, in all references it’s sulfuric while you use sulphuric, consider changing throughout the text for consistency.

Fig. B8: After this figure, or in the main text, I’d recommend to add a composite figure that will include all the results of onset saturation ratio with respect to ice freezing where 1 % of the aerosol particles are activated as a function of temperature.

Fig. C3: what are the implications of these charts on the ice nucleation results and analysis? A discussion is missing in the main text.