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Interactive comment on "The Role of Contact Angle and Pore Width on Pore Condensation and Freezing" *by* Robert O. David et al.

Anonymous Referee #1

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David et al. present ice nucleation measurements with well-characterized porous silica particles to investigate the efficiency of the pore condensation and freezing (PCF) ice formation pathway as a function of the particles' pore diameter, contact angle, and surface functionalization. The reported ice nucleation behavior is generally in agreement with that predicted by the inverse Kelvin equation, which is the starting point to theoretically describe the PCF mechanism. In some cases, further considerations, like limited growth time of ice crystals in the ZINC CFDC and pressure-dependent homogeneous ice nucleation rates, were taken into account to fully explain the experimental observations. It therefore remains challenging to derive a general parameterization of the PCF mechanism for e.g. ambient dust particles, but the experiments presented in this manuscript with the synthesized particles are an important step to understand which

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Discussion paper

factors control the ice nucleation behavior of porous particles. A particular strength of the study is the comprehensive characterization of the particles with a number of different techniques as presented in Sect. 3.1. The manuscript itself is well-structured and in most parts clearly written. Reading the discussion of the ice nucleation measurements, however, was sometimes a bit challenging due to the variety of explanations taken into account to reconcile the findings with theory. I suggest below a couple of points which would need further clarifications, but otherwise recommend the publication of this article in ACP.

Specific comments:

1) Page 13, line 7: How did you exactly infer the range of contact angles for a given MCM-41 sample as also listed in Table 1 – did you use the uncertainty of d_DFT listed in Table 1, thus using e.g. pore diameters between 3 and 3.6 nm for the 3.3M1 sample in the calculation?

2) Page 13, line 12: Concerning the difficulty in the assignment of the “correct pore diameter responsible for the *initial* pore condensation”: This statement seems to me a bit in contradiction with the one on page 6, line 14/15, saying that you did not use the onset relative humidity in the water sorption isotherms to compute the contact angle but the value where the pore condensation step is the steepest. So, the average pore diameters listed in Table 1 should be a reasonable choice for the computation and not the lowest value of e.g. 7 nm for the SBA-15 samples.

3) Page 14: I have a couple of questions regarding the DSC measurements: Is there an influence of external ice on the initiation of freezing in the pores (in the caption of Fig. 4 you use the expression “ice growth into pores”? Did you also record the DSC thermograms during heating, are the peak positions different from the cooling runs? How do your results compare with previous DSC measurements for MCM-41 and SBA-15 as e.g. summarized in Marcolli (2014)?

4) Page 16, line 22/23 & page 26, line 27: The reference to Skrotzki et al. (2013) does

not agree with the choice of an accommodation coefficient as low as 0.1 to compute the ice growth. As far as I can see, Skrotzki et al. (2013) reported accommodation coefficients > 0.2 for all conducted experiments with an overall average value of 0.7. So, I am not fully convinced that the limited ice growth is the best explanation for the absence of immediate ice growth as soon as ice saturation is reached in ZINC. The authors discuss on page 17 that a non-negligible fraction of the aerosol might experience a lower supersaturation than computed for the center of the aerosol lamina in the CFDC - this might also explain in part the higher onset values for ice growth on the 2.8C2 and 2.8H2 particles. Also, the onset RHi values are given for an already quite high ice-active fraction of 5%. In the full ZINC scans for 2.8H2 in Fig. A1 a and b one can see that the ice growth initiates clearly below 110% RHi – so not too far from the expected value of 100% RHi if also considering the RHi uncertainty in ZINC. Did the particles enter ZINC in a dry air flow (without pre-condensed water in the pores) – could this also influence the ice nucleation measurements?

5) Page 16, line 25 and page 26, line 24: The reference to Järvinen et al. (2016) also does not seem appropriate for me to justify a spherical shape of ice particles in the computations. They observed “quasi-spherical” ice crystals from the freezing of water droplets during strong convection, which is a clearly different process from growth of ice crystals on near-spherical solid silica particles as in the present study.

6) Page 18, line 22ff, discussion related to the increase in the AF to 0.02 for the 2.8H2 sample up to RHi = 120%. I am a bit confused by this paragraph: In the preceding paper by David et al. (2019) in PNAS, the authors show in Fig. 2 the ZINC scans for porous MCM-41 particles with 3.8 nm pore diameter. This pore diameter should be large enough to host a critical ice germ at 233 K. But in the ZINC scan at -40°C, ice formation did not occur below water saturation, and was explained by the fact that the homogeneous ice nucleation rates are not large enough to observe ice within the residence time of ZINC. If you applied the same argumentation with the pressure-dependent parameterization of CNT as presented in the current manuscript, why didn’t

you detect any freezing signal for the 3.8 nm pore diameter particles at low RH? Could the small freezing signal for the 2.8H2 sample at lower RH not simply be due to immersion freezing within the pores? If I understood correctly, you used this explanation for the freezing signal observed for the 9.0M2 particles at 233 K (Fig. A2c and page 22, lines 24-27). The ZINC scan at 238 K with the 2.8H2 particles shows that at least the external particle surface contains active sites for condensation or immersion freezing (page 19, line 4/5). In contrast, the 3.8 nm pore diameter particles did not reveal a distinct immersion freezing signal at -35°C (Fig. 2 in David et al., 2019).

7) Page 21, lines 5-13: See above, would a pressure dependent parameterization of CNT not also predict a strong increase in AF for the 3.8 nm pore diameter particles at 233 K and low RH? If you also plotted the active fraction curve for the 3.8 nm pore diameter particles at 233 K from David et al. (2019) into Fig. A1c (hydroxylated and calcined samples seem to behave rather similar, see Fig. 5), the 3.8 nm sample would not show an “intermediate” ice nucleation behavior between that of the 9 nm pore diameter and that of the 2.5 – 3.3 nm pore diameter particles, but just reveal a very low ice-active fraction until reaching water saturation. How would you interpret this difference?

Minor comments and technical corrections:

1) Page 1, line 11: Maybe explicitly state “due to the inverse Kelvin effect”

2) Page 1, line 14 + 17: Avoid the repetitive statements “play an important role in determining the relative humidity” and “play an important role in predicting the humidity” in the abstract. Instead, you could also mention what type of chemical functionalization was employed and its effect on the ice nucleation behavior.

3) Page 2, line 28: “is the interfacial energy”

4) Sect. 2.1.2: You should already indicate here the larger pore sizes of the SBA-15 particles compared to MCM-41.

5) Page 5, line 4: Missing parenthesis ")" after "60°C".

6) Page 6, line 13/14: Could be phrased more clearly, you could also indicate the respective values for bulk water as a comparison.

7) Sect. 2.4: What was the relative humidity of the air before entering ZINC? Please indicate.

8) Fig. 1b & 2b: It is hard to discriminate the various bluish colors.

9) Page 12, line 4: You could also mention here in the text that you did a series of two adsorption/desorption cycles with the samples.

10) Page 12, line 19: "The relative mass . . . does not return"

11) Page 14, line 18: Maybe: "By contrast, the freezing temperature . . ."

12) Page 16, line 22: "peach" lines vs. "salmon" lines used in the caption of Fig. 5.

13) Page 17, line 3 (second line in figure caption): Could you please briefly include the factors contributing to the RHi uncertainty in ZINC?

14) Page 17, line 9: "an AF_0.05"

15) Page 21, line 25/26: Please check sentence structure.

16) Page 25, line 18 – 20: Please check sentence structure (avoid to use twice sub-clauses with "while").

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