Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Evolution of confined ice nano structure at different levels of pore filling: A Synchrotron based X-ray diffraction study

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SUPPLEMENTARY INFORMATION

The supplementary information contains

i) Figuresfrom S1 to S3
ii) Appendix I: DSC result hydrated MCM-41 pores at 70 and 40 % pore fillings
iii) Appendix II: XRD pattern of dry MCM-41 matrix at different temperatures
iv) Appendix III: Fitting of the diffraction peaks

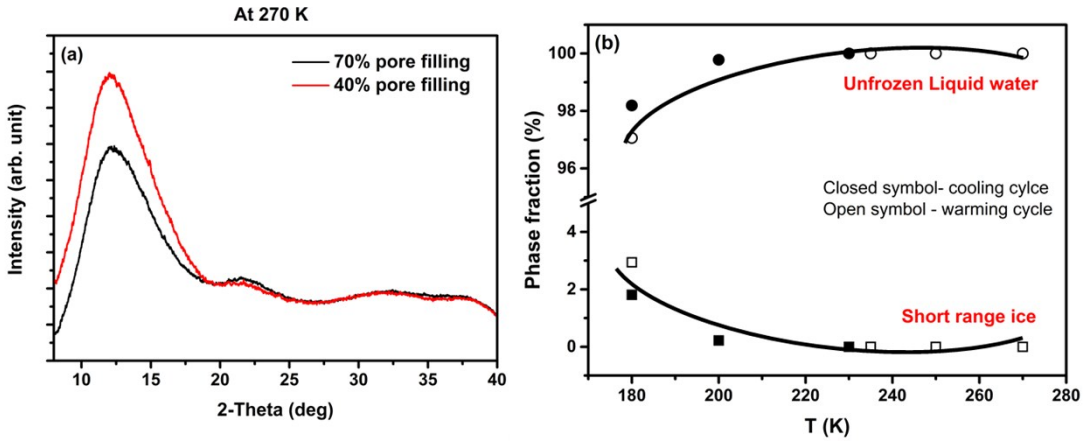

Figure S1. (a) Comparison of diffraction pattern obtained at 270 K for 70 and 40 % pore fillings and (b) Phase fraction at 40 % pore filling at different temperatures during cooling and warming cycle. The lines drawn through the data points are only for eye-guides.

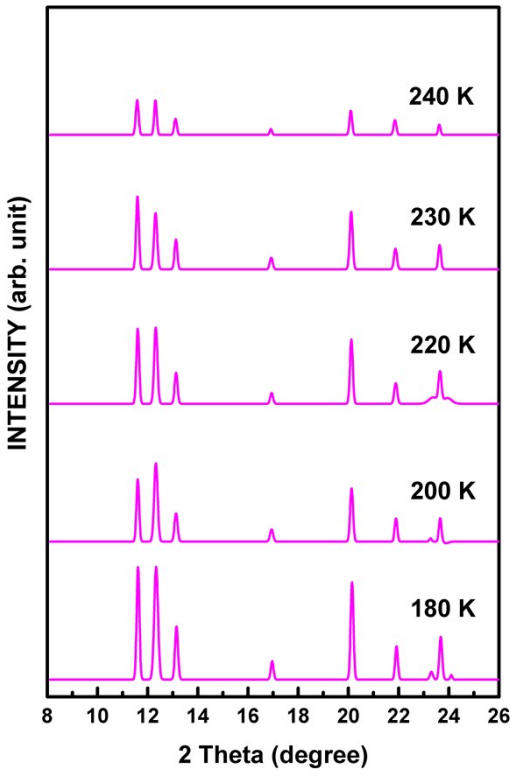

Figure S2. Diffraction peaks of crystalline ice extracted by subtracting the short-range ice and liquid fraction (obtained by fitting) from the observed diffraction pattern for 70 % hydrated MCM-41 at different temperatures during the cooling cycle.

Appendix I: DSC result for hydrated MCM-41 pores at 70 and 40 % pore fillings

Differential Scanning Calorimetry (DSC) measurements were carried out to observe the phase transition of water at both the hydration levels and to ensure the absence of excess/surface water. About 30 mg of the hydrated sample was weighed and sealed in an Aluminium crucible. Mettler Toledo DSC823 Calorimeter was used for the measurements during the cooling-warming cycle at static air condition to determine the freezing and melting temperatures. The measurements were carried out over the temperature range of 300K to 150K at a scanning rate of 10Kmin^{-1}.

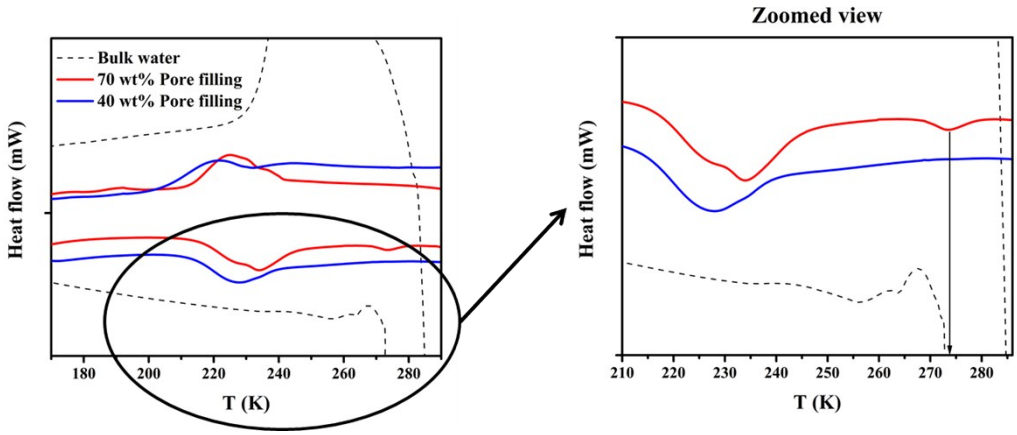

Figure S3.DSC thermograms for water confined in MCM-41 at 70 and 40 % pore filling along with bulk water. The right panel shows the zoomed view of the melting cycle. The dashed arrow at 273K in the right panel represents the melting of ice.

The DSC thermograms of 70 and 40 % hydrated MCM-41 is shown in Figure S3 along with the bulk water. The DSC thermogram of bulk water shows an endothermic peak at 257K (ΔT_f = 16K) during the cooling cycle and an exothermic peak at 273K during the warming cycle. The shift in the freezing point of the bulk water is due to supercooling of water. DSC thermogram of dry MCM-41 shows no transition in the desired temperature range i.e. 300 to 180 K (data not shown). A broad endothermic peak at nearly 230 - 220 K is observed for both the hydration levels during the cooling cycle and attributed to crystallization of water inside the pores. During the warming cycle, the transition occurred at 227 and 234 K for 40 and 70 %, respectively. The transition at 227 and 234 K is assigned to the melting of the ice inside the mesopores of MCM-41. There is no sharp transition near to bulk freezing/melting temperature indicating absence of bulk-like water, which could be present outside the pores. However, a small exothermic peak at 273K is observed at 70 % hydration during the warming cycle. However, this peak is absent in the case of 40 %

hydration level. This shows that the bulk-like water is present in very small amount in the case of 70 % hydration and absent in 40 % hydrated pore.

Appendix II: XRD pattern of dry MCM41 matrix

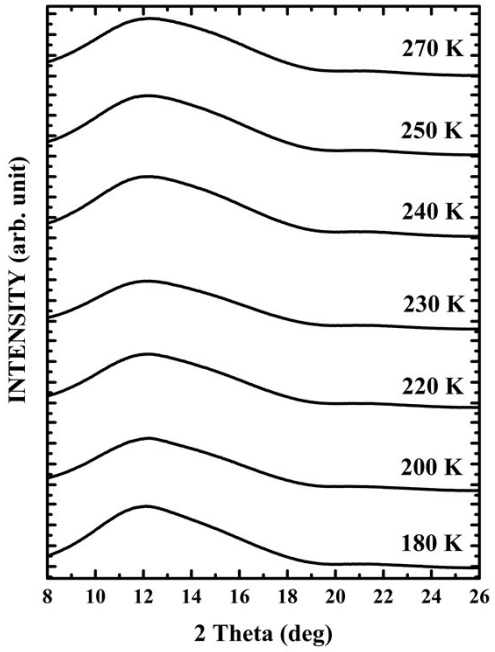

Figure S4.XRD pattern of dry MCM-41 matrix at different temperatures.

The XRD pattern shown in figure S4 reveals a single broad peak in the 2θ angle range of interest. It implies the amorphous nature of the MCM-41 matrix. The peak corresponding to uniform hexagonal array of pores is generally observed at 2θ angle less than 5 degree.[1] With the present experimental set-up, the measurements at low angle could not be done. The low angle peak does not coincide with diffraction peaks of confined ice and therefore, would not affect the present analysis. The diffraction pattern of the confined sample comprises of the contribution from dry matrix. The pattern of dry matrix is subtracted from the confined sample pattern to get the contribution from confined water.

Appendix III: Fitting of the diffraction peaks

Matching of the diffraction pattern at 270K was done initially to formalizethe approach to fit the diffraction pattern of liquid water. The diffraction patternof confined water was best fittedwith a linear combination of four broad peaks having Gaussian line shape over

the range of 2Θ = 8°-26°.[2] The shape of the broad diffraction pattern was fixed for the subsequent fittings to obtain the fraction due to unfrozen liquid water.[2] The same methodology was used to get the best fit of the pattern at 250K. The experimental pattern was best fittedwith the pattern of water at 270 and 250 K. At 240K, presence sharp peaksindicates freezing of water. Therefore, the fitting the fitting of the experimental diffraction pattern required additional sharp peaks (2Θ = 11.6°, 12.3°, 13.1°, 17.0°, 20.1°, 21.9° and 23.7°) along with the broad peak due to liquid water. From 240 to 220K, the XRD pattern gave best match just by decreasing the intensity of broad peak and increasing the heights of sharp peaks. Below 220K, two additional sharp peaks occur at (hkl) corresponding to (200) and (201) of hexagonal phase. Therefore, the matching at temperatures lower than 220K required additional two sharp peaks with Gaussian line shape. The fittings were quite good till the 230K but gave a poor match at 220, 200 and 180 K. Below 220 K, there was a need for three additional broad peaks at 2Θ approx. 12°, 20° and 24° other than liquid fraction and crystalline ice to get the best fit of the observed XRD pattern. These peaks were broader as compared to crystalline ice and occurred at characteristic Bragg angles. Fitting of220, 200 and 180 K spectra weredone by considering the contribution from three components i.e. unfrozen liquid water, crystalline ice and an additional phase with 3 peaks. The peak positions of three additional peaks match with the positions for Ice I_c with a very broad peak width as compared to that of calculated peak. The broad peak width can be correlated to the small crystallite size. Therefore, this additional fraction can be assigned to a fraction of ice which is cubic like with a very small crystallite size. The area under the sharp (crystalline) peaks and the broad peaks (unfrozen liquid and cubic like ice) fitted by above method was obtained to get the phase fraction.

References:

1. M. Kruk, M. Jaroniec, J. M. Kim and R. Ryoo, *Langmuir*, 1999, **15**, 5279–5284.
2. K. Morishige, *The Journal of Physical Chemistry C*, 2018, **122**, 5013–5019.