Captions for supplement figures

Fig. 1. (a) Reproducibility of DSC measurements of water contacted with SBA-16(80).

Runs 1–4 were conducted at a rate of 5 K min⁻¹, run 5 at 10 K min⁻¹, and run 6 at 5 K min⁻¹.

(b) Effect of scanning speed and reproducibility of DSC measurements of water contacted with S-16(120). Runs 1 to 6 were conducted sequentially at 5, 10, 7, 5, 2, 5 Kmin⁻¹. Coincidence of the runs 1, 4, and 6 at 5 Kmin⁻¹ substantiates the reversibility of the freezing and melting processes of confined water. Freezing temperatures were lowered with increase in cooling speed, while melting temperature were almost unvaried up to 7 Kmin⁻¹; very small shift was seen with 10 Kmin⁻¹ which is probably due to the delay of thermal conduction between the stage for the sample and the sample pan.

Fig. 2. The adsorption–desorption cycles of water on (a) S-15(100), (b) S-16(80), and (c) S-16(120) at 298.2 K. The measurements were cycled along the desorption direction after the adsorption to saturation of pores and the desorption below the closure point of hysteresis pressure and adsorption up to capillary condensation.

(a) Each desorption curves from different capillary condensation range run separately down to closure point around at RP =0.5 in the capillary
condensation region, indicating that adsorption-desorption process separately in all the cylindrical pores.

(b) Each desorption curve run in parallel with each other down to the pressure for cavitation desorption around at $RP=0.35$, at which condensed water is evaporated in any run. This indicates that filling of water occurs from pore to pore.

(c) Separate desorption runs, 2, 3, 4, 5 from capillary condensation range are those for cylindrical pores. After closing around at $RP=0.55$, isotherms run on the same line to cavitation desorption around at $RP=0.38$, indicating that some proportion of small spherical pores is detectable with water vapour adsorption.

Fig. 3. XRD patterns of water confined in S-16(120): (a) cooling, (b) warming. X-rays used were MoKα (the wavelength of 0.07107 nm).

Fig. 4. DSC curves of water contacted with S-16(45)—effect of the amount of dosing water. The numbers with “ad” signify the dosing $RP$ along the adsorption direction, and those with “des” along the desorption direction. The broken line drawn for the cooling curves is for the homogeneous nucleation temperature of
water (HNT).
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(a) 5th run, 10 Kmin⁻¹

1,2,3,4,6th run, 5 Kmin⁻¹

T

T/K

ENDO → EXO

200 210 220 230 240 250 260 270
2nd run, 10 Kmin^{-1}
3rd, 7 Kmin^{-1}
1, 4, 6th, 5 Kmin^{-1}
5th, 2 Kmin^{-1}

External water