Can the compressibility of mesoporous silica be measured from nitrogen adsorption and mercury porosimetry?

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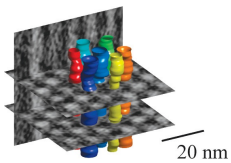
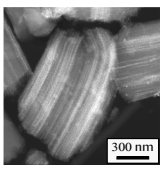
SBA-15 ordered mesoporous silica

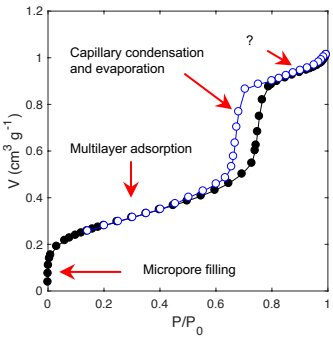


Cylindrical mesopores are small scale [1]

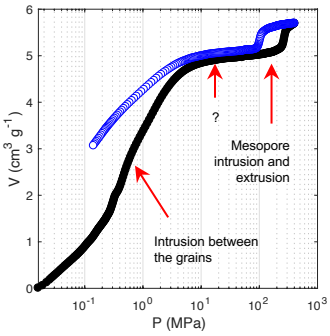


Grains at large scale [2]

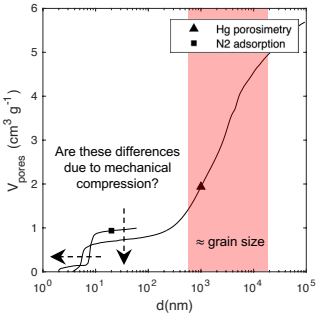
Nitrogen adsorption



Mercury intrusion



Pore-size distributions

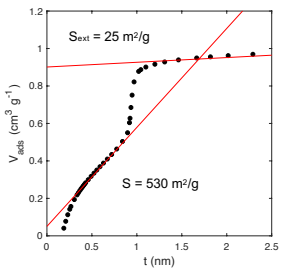


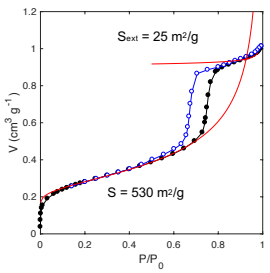
Globally, nitrogen adsorption and mercury porosimetry consistently testify to mesopores slightly smaller than 8 nm and to grains larger than a few micrometers.

Can the small differences between the two techniques be interpreted in terms of compressibility?

Nitrogen adsorption data analysis

Adsorption on the outer surface of the grains ?



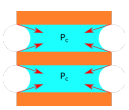


The estimated "outer surface area" of 25 m²/g converts to a size of 200 nm, which is much smaller than the grains.

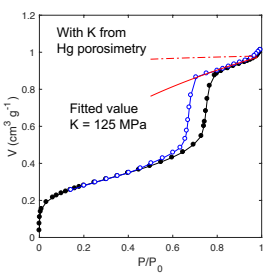
Compression of the grain by capillary forces?

The menisci at the pore mouth compress the solid.

$$P_c = \frac{RT}{V_m} \ln\left(\frac{P}{P_0}\right) \simeq 6 \text{ MPa}$$



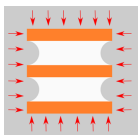
$$\frac{V}{V_0} = \left(\frac{P}{P_0}\right)^{\alpha} \text{ with } \alpha = \frac{RT/V_m}{K}\frac{1-\epsilon}{\epsilon}$$



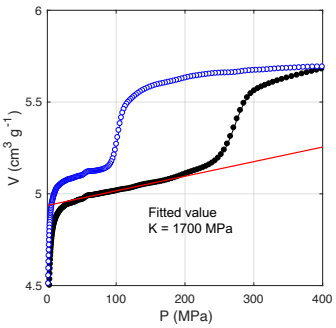
Compression alone cannot explain the data, unless the material is assumed to be unrealistically soft.

Mercury porosimetry data analysis

Before intrusion, the mercury compresses the solid.



$$V_{Hg} \simeq V_G \times \frac{P}{K}$$



The published values for the compressibility range from about 1600 MPa [3, 4] to 7000 MPa [5]. Our value from mercury porosimetry is close to the lower limit, but it is realistic.

Conclusions

- Mercury porosimetry provides a realistic value for the bulk compressibility of SBA15;
- The 20% compression of the grains before intrusion also explains well the difference between pore size distributions from nitrogen adsorption and mercury porosimetry;
- One can rule out any significant effect of compressibility for the nitrogen adsorption;
- Still, the high-pressure adsorption cannot be explained by the outer-surface of the grains alone;
- Does capillary condensation occur at the contact point between grains?

[1] Gommes et al. "Quantitative characterization of pore corrugation in ordered mesoporous materials using image analysis of electron tomograms" Chem. Mater. 21 (2009), pp. 1311-1317;
[2] Gommes et al. "Small-angle scattering analysis of empty or loaded hierarchical porous materials", J. Phys. Chem. C 120 (2016), pp. 1488-1506;
[3] Galarneau et al. "Pore-shape effects in determination of pore size of ordered mesoporous silicas by mercury intrusion", J. Phys. Chem. C 112 (2008), pp. 12921-12927;
[4] Balzer et al. "Relationship between pore structure and sorption-induced deformation in hierarchical silica-based monoliths", Z. Phys. Chem. 229 (2015), pp 1189–1209;
[5] Prass et al. "Capillarity-driven deformation of ordered nanoporous silica", Appl. Phys. Lett. 95 (2009) 083121;