Supercritical Drying of SiO_2 and ZrO_2 Aerogels

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Introduction

Aerogels are nano-porous, fractal-like structures. They have unique structural properties such as high **thermal insulation** and high **inner surface areas**. Aerogels can be produced by drying of wet gel structures, containing residue reactant and solvent in their cavities. Conventional drying give rise to **capillary forces** in the nanoscale cavities and the structure collapses. A way of circumventing this problem is by applying **supercritical drying**. [1]

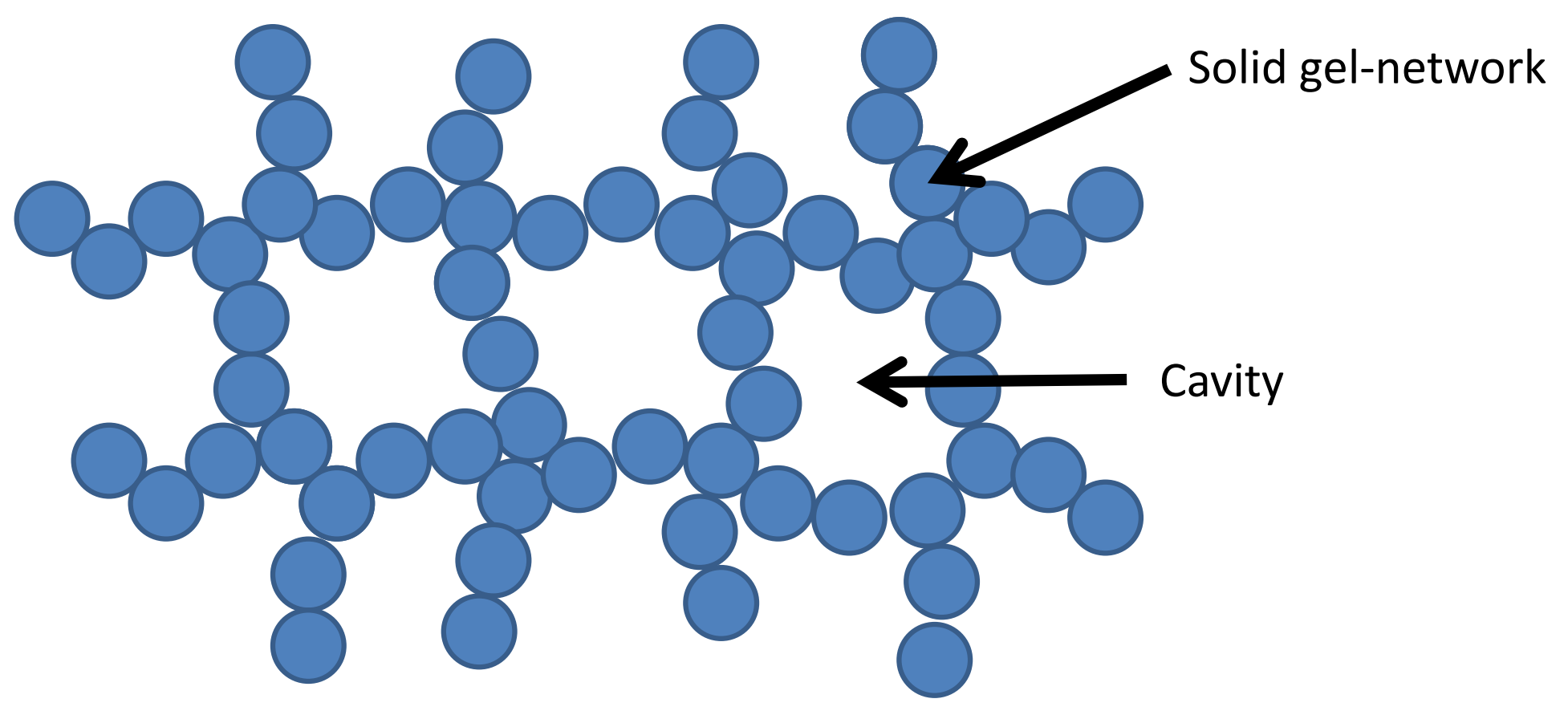

Figure 1: A graphical representation of a non-specific gel-structure.

Experimental

Supercritical fluids have properties resembling both gas and liquid at the same time. An interface between a supercritical liquid and a gas or liquid is therefore not associated with any interface energies, thereby **eliminating the cause of capillary forces**.

The general procedure for a supercritical drying consists of **3 steps**.

1. Substitution of the residue reactant and solvent with liquid CO_2
2. Applying pressure and heat to reach the supercritical point of CO_2
3. Releasing the supercritical CO_2 as gas without any shrinkage of the gel

After these 3 steps one has a **final and fully-functional aerogel**.

The experimental setup used for supercritical drying is shown schematically in figure 2. Aerogels composed of respectively $\mathbf{SiO_2}$ and $\mathbf{ZrO_2}$ have been synthesized using this setup.

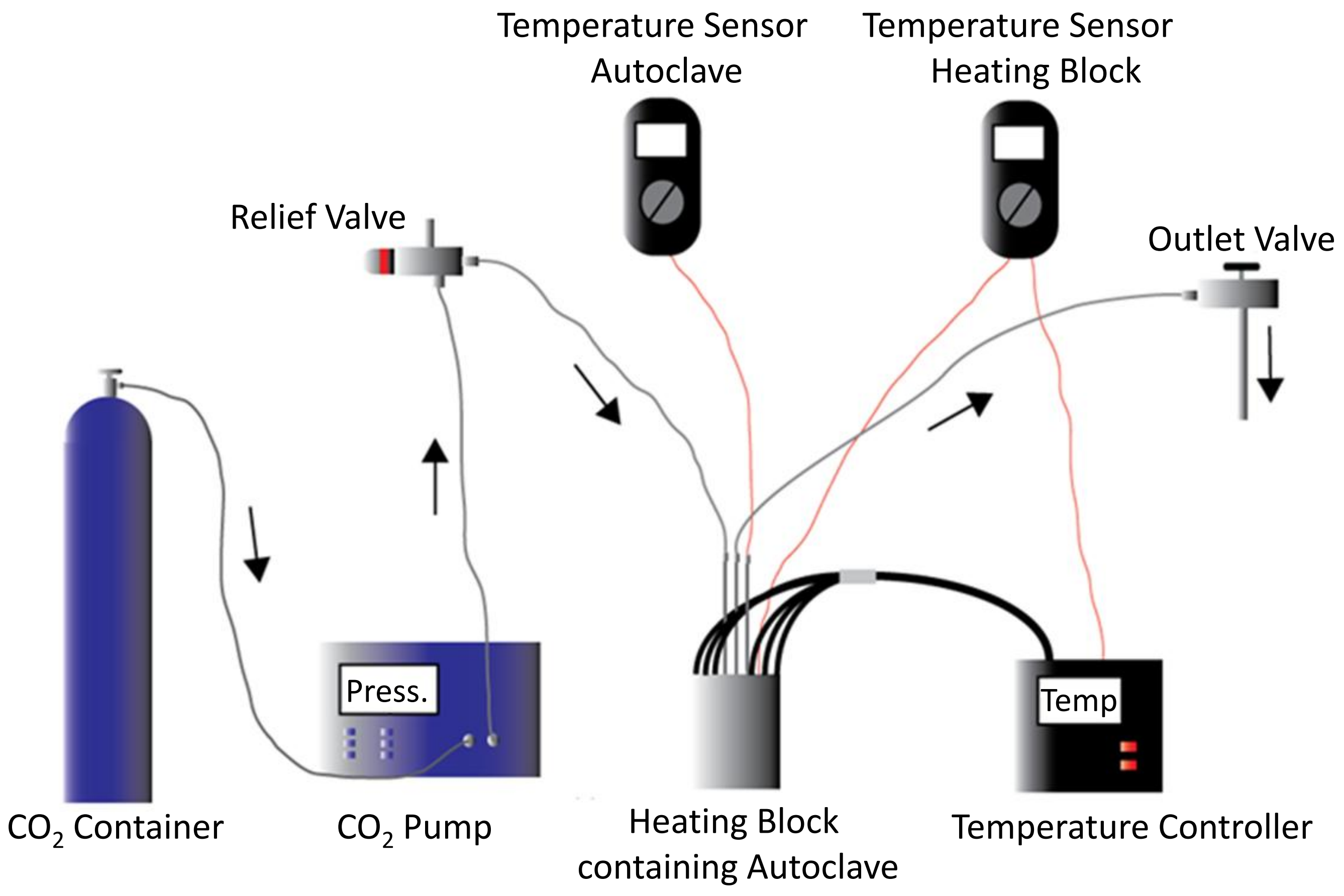

Figure 2: The experimental setup used for supercritical drying of wet gel structures.
The arrows shows the flow of the supercritical fluid during operation.

Results

The final aerogels were analyzed using the **Brunauer-Emmett-Teller (BET)**[2] theory to determine the specific surface area and the pore size distribution

The results for some selected gels, diversified and dried under different conditions are shown to the right.

It can be seen that when it comes to **larger surface area** and **smaller pore radius**, the gels dried under supercritical conditions are superior to the same kind of gels dried under atmospheric conditions

The SiO_2 gel with the highest surface area is not dried supercritically. Instead it has undergone **surface modification** with TMCS. This technique is known to give very high surface areas but the pore radius equally grows because of the surface molecules.[3]

Surface area for SiO_2 aerogels

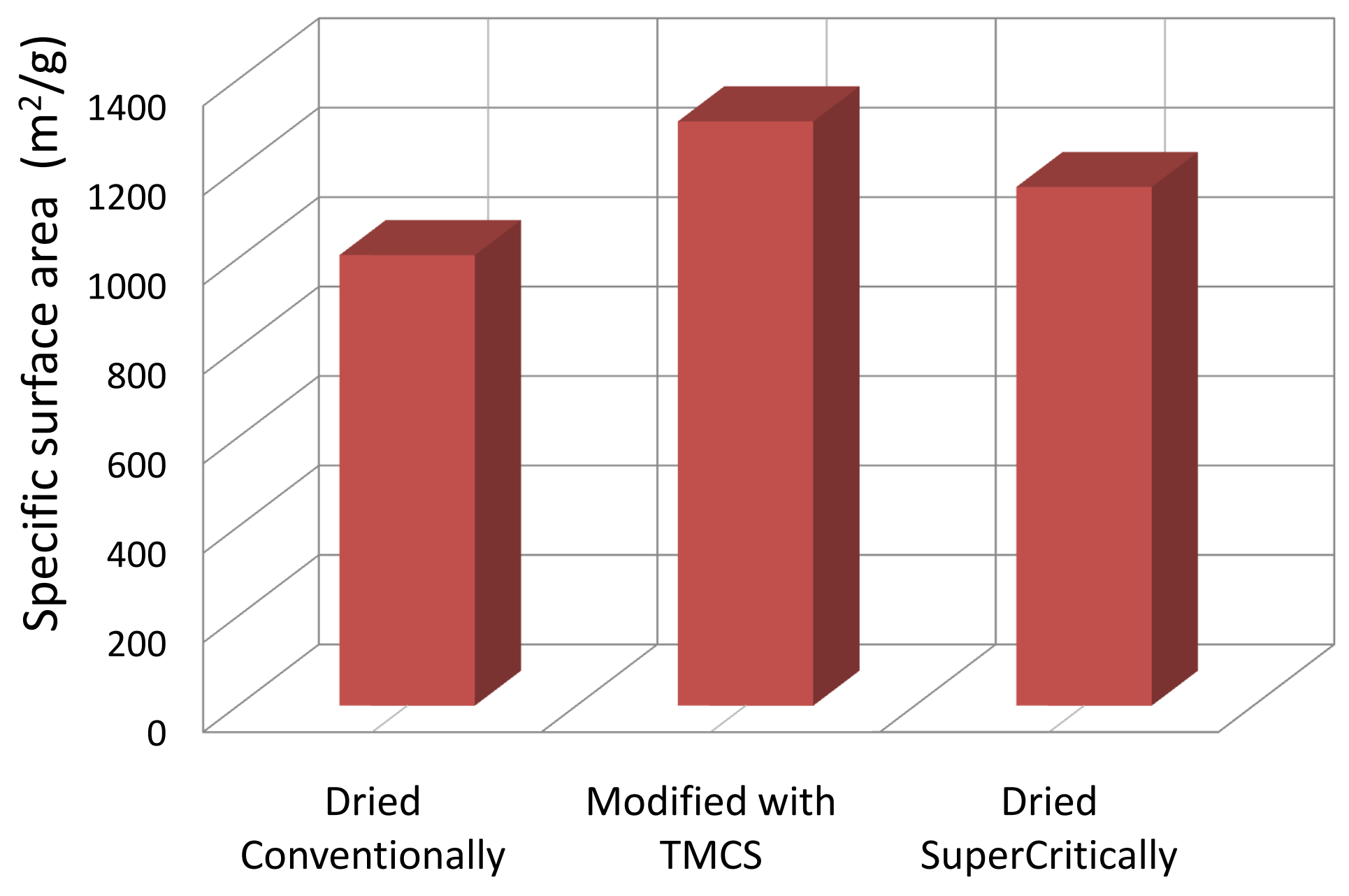

Figure 3: The inner surface areas for different SiO_2 aerogels. The center bar represents a gel modified with trimethylchlorosilane as a surfactant.

Surface area for ZrO_2 aerogels

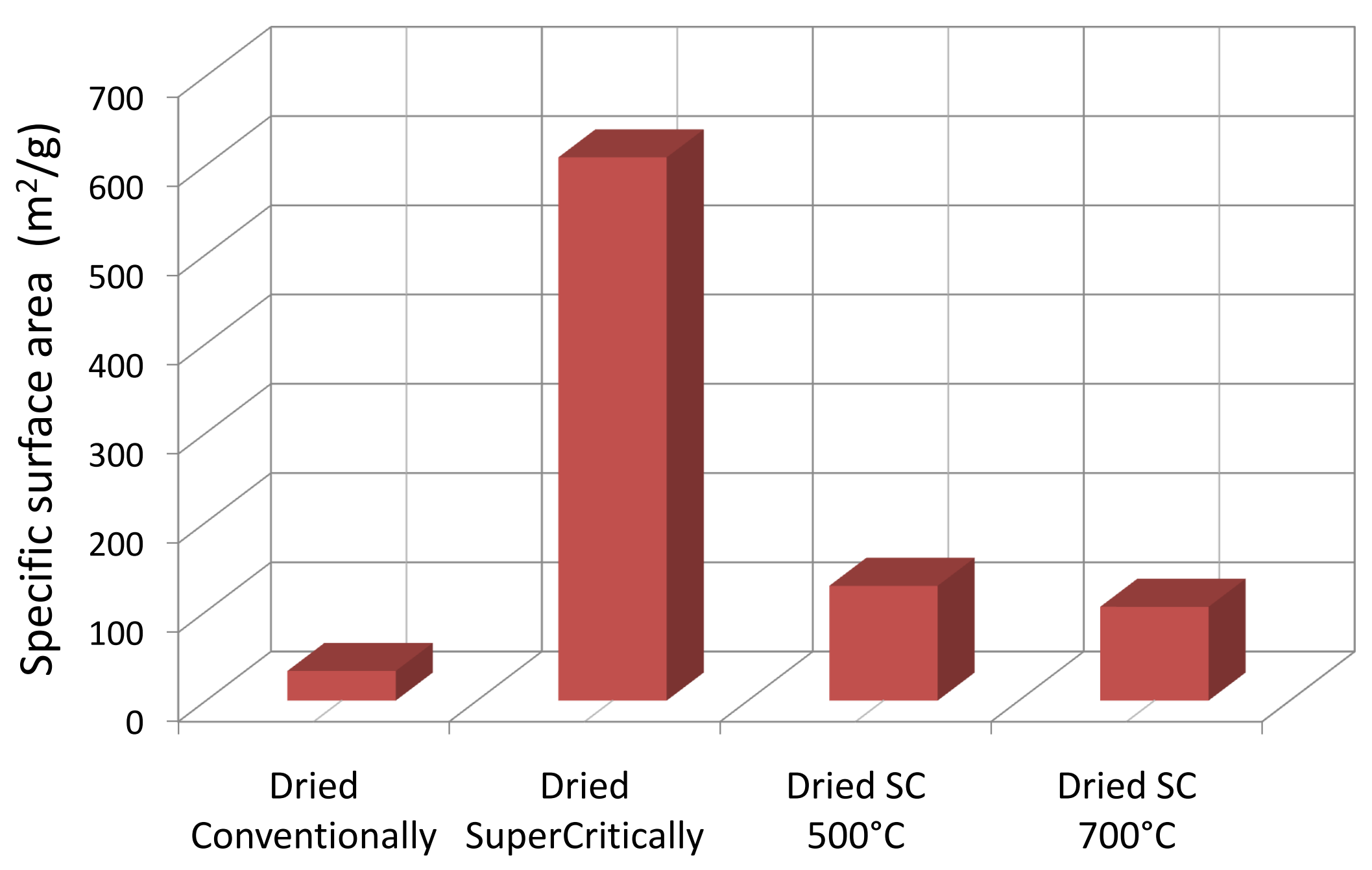

Figure 5: The inner surface areas for different ZrO_2 aerogels. The two last columns represents gels that have been dried SC and thereafter been heated to 500 ˚C and 700˚C

Pore distribution for SiO_2 aerogels

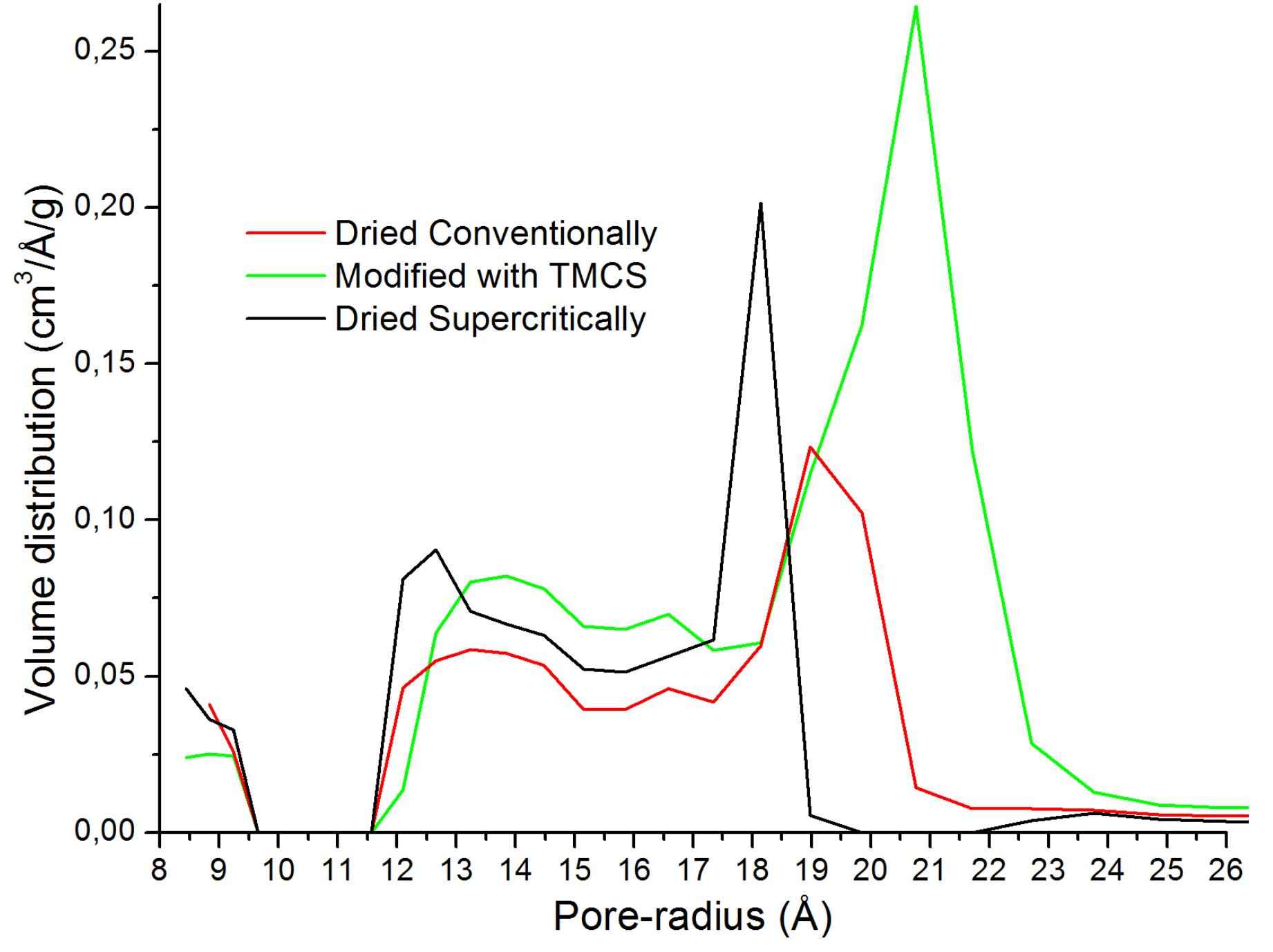

Figure 4: The pore distribution of different SiO_2 aerogels. The most likely pore-radius is smaller for the SC dried gel than for the other two gels.

Pore distribution for ZrO_2 aerogels

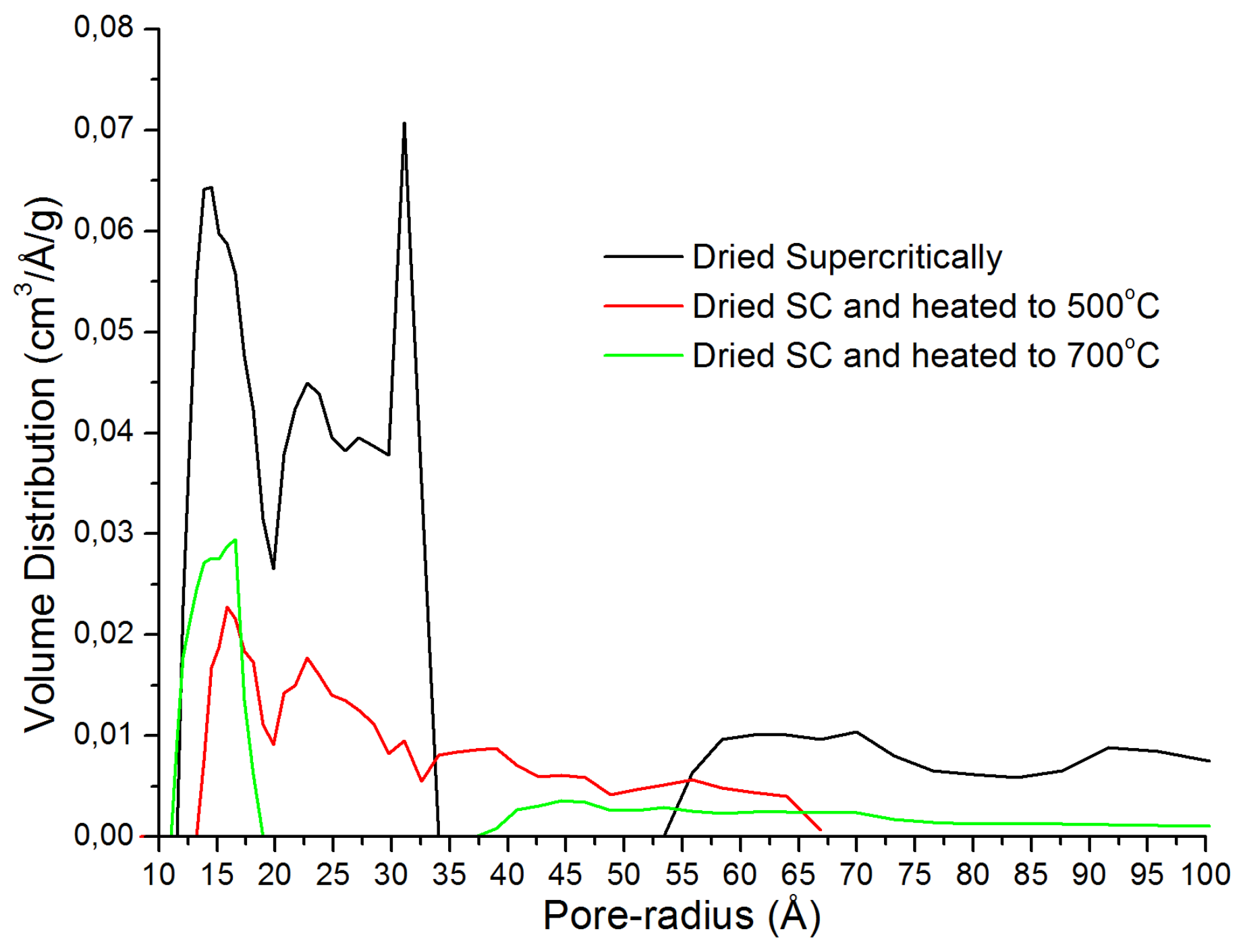

Figure 6: The pore distribution of different ZrO_2 aerogels. It is seen that the pore distribution gets narrower when the gel is heated. The conventional gel was too compact to measure the pore distribution.

Conclusion

The results presented here shows that when using supercritical drying more of the original characteristics of the wet gel are preserved. This gives **larger inner surface areas** and **smaller pore radii** among other interesting structural properties.

There is a large difference on the effect of SC drying when comparing the results from different gel materials. These can be explained with a difference in strength of the wet gels before any drying. It is clear that **Supercritical Drying is a useful tool for drying samples with a very fragile microstructure.**

[1] Aerogels- Airy Materials: Chemistry, Structure, and Properties ; Nicola Hüsing, Ulrich Schubert ; Angew. Chem. Int. Ed., 1998, 37, 22-45
[2] Adsorption of Gases in Multimolecular Layers; Stephen Brunaer, P. H. Emmett, Edward Teller; Journal of the Am. Chem. Soc., 60, 309-319
[3] High specific surface area TEOS-based aerogels with large pore volume prepared at an ambient pressure; Pradip B. Sarawade, Jong-Kil Kim, Ho-Kun Kim, Hee-Taek Kim; App. Surf. Science, 254, 574-579

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