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# Design of steam-stable silica membranes

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## 1. $H_2$-selective silica membranes

Silica membranes for hydrogen separation are asymmetric systems consisting of a macroporous support, an intermediate mesoporos layer, and a thin gas-selective top-layer. The typical structure of a silica membrane is shown in Figure 1.

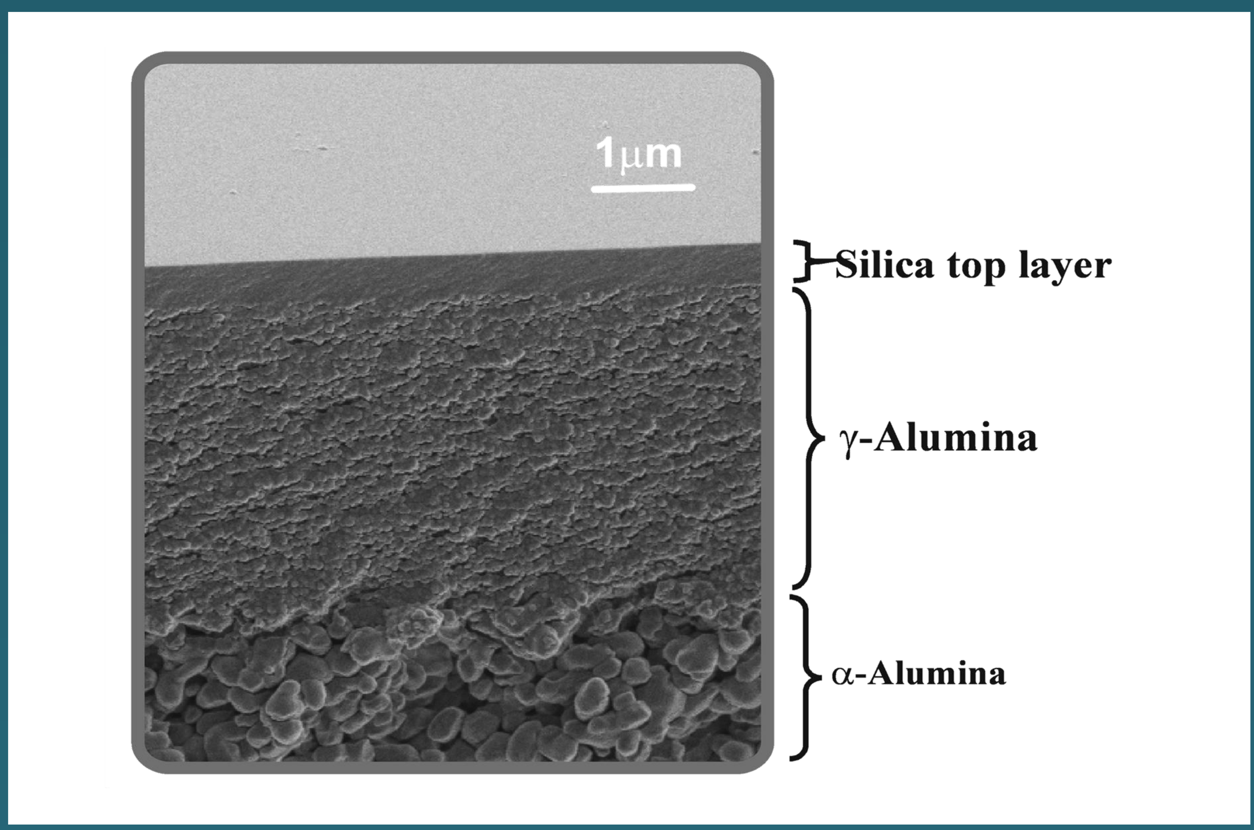


Figure 1. SEM picture of a $H_2$-selective silica membrane.

These membranes allow separating the small hydrogen molecules from larger molecular species, as $CO_2$ and $CH_4$ (Figure 2). Therefore, these devices appear to be promising for the future hydrogen-based economy.

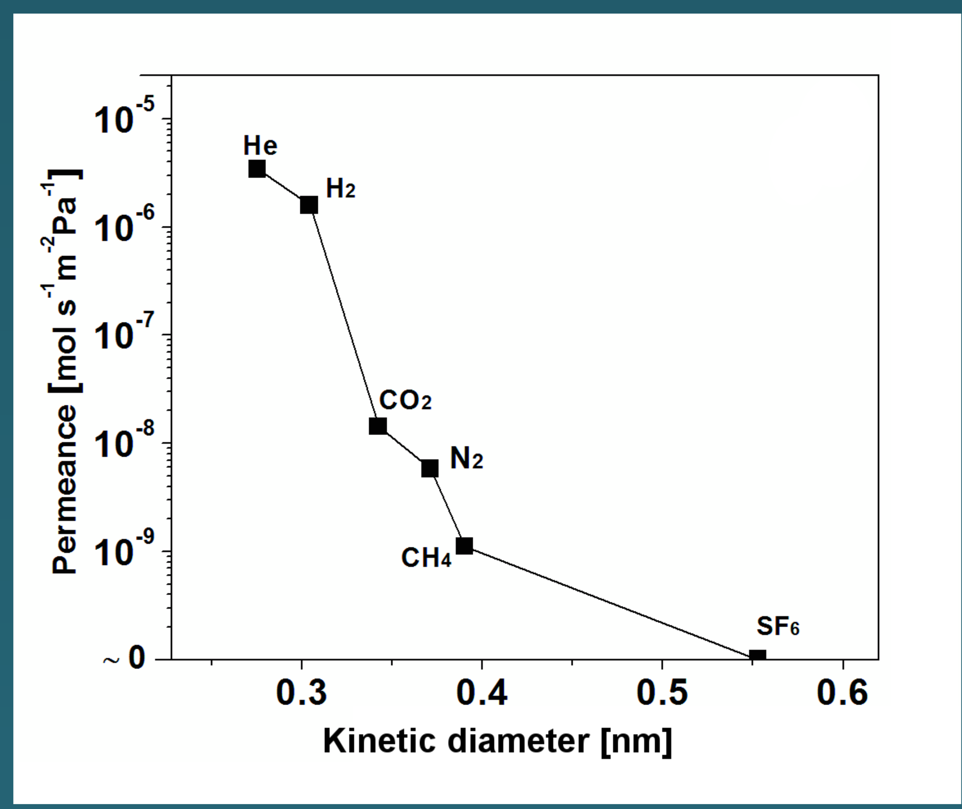


Figure 2. Permeance values of various gases through a silica membrane.

## 2. Hydrothermal instability

However , several works report poor stability for this membranes in presence of steam at temperature as low as 60 °C. As shown in Figure 3, during hydrothermal exposure, the porous silica structure collapses, yielding a denser material with a consequent loss in membrane permeability and selectivity.

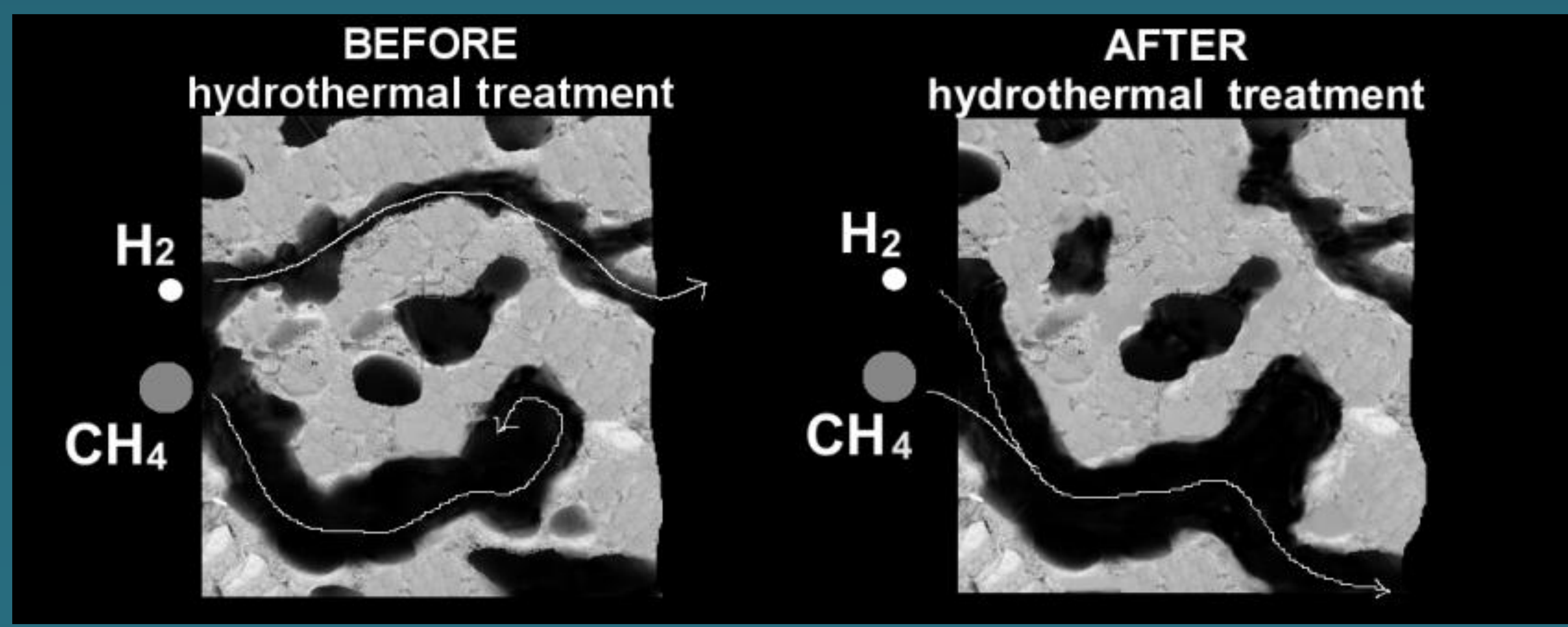


Figure 3. Representation of the structural changes in a silica membrane due to hydrothermal exposure.

## 3. Modified silica membranes

Silica networks can be stabilized by doping. In this work Ti(IV), Zr(IV), and Nb(V) ions were used to stabilize silica membranes. A pore forming agent was applied to obtain materials with different composition but similar pore structure. After hydrothermal exposure, the unsupported membranes presented a lower pore volume, a lower surface area and a broader pore size distribution. Densification was less pronounced for the doped membranes than for the pure silica reference sample (Figure 4). The gel-to-glass transition ($T_{peak}$) and the glass transition ($T_g$) temperature were determined by calorimetric analysis (Figure 5). As shown in Figure 6, a good correlation was found between the glass transition temperature of these materials and their surface area loss due to steam-exposure. The higher glass transition temperature and the enhanced hydrothermally stability of the doped samples can be considered as a result of the higher network connectivity.

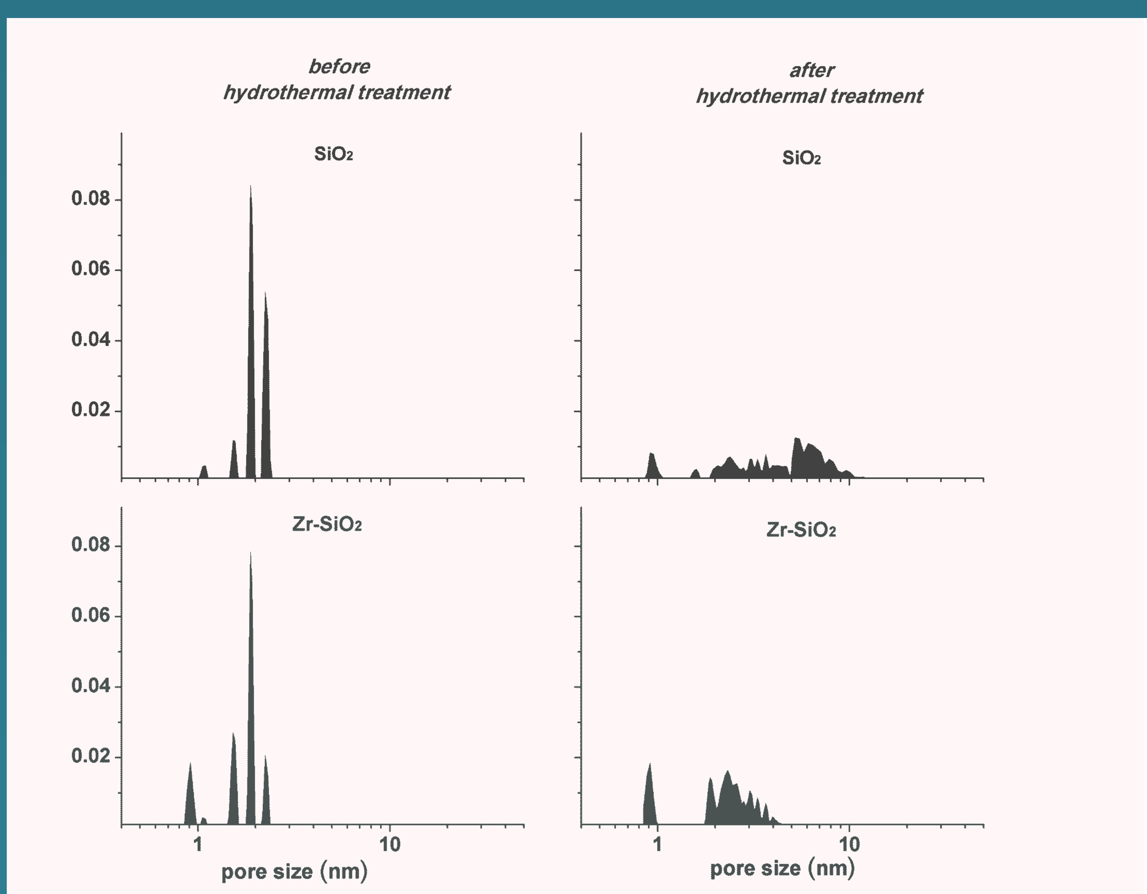


Figure 4. Pore size distributions of a pure silica and of a 5% $ZrO_2$- doped silica membrane before and after hydrothermal treatment.

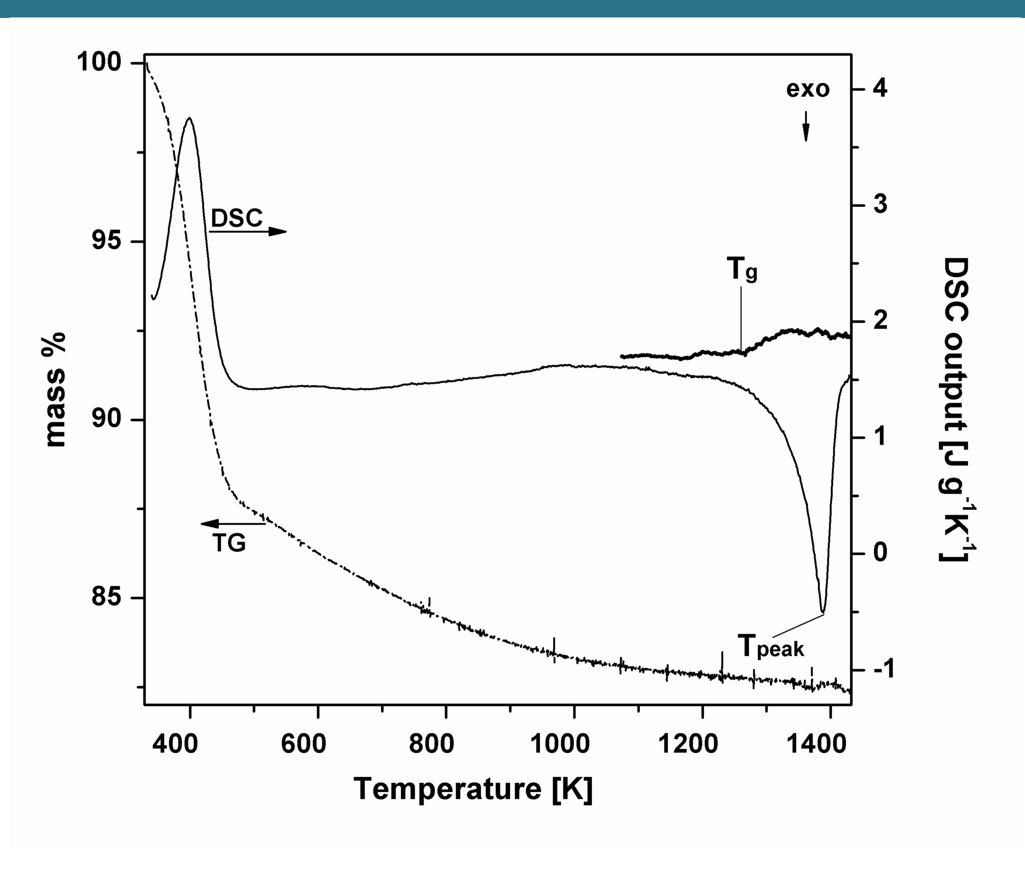


Figure 5. TGA (dashed line) and DSC (solid lines) of an unsupported membrane after calcination at 723 K for 18 h (thin lines) and at 1373 K for 24 h (thick line).

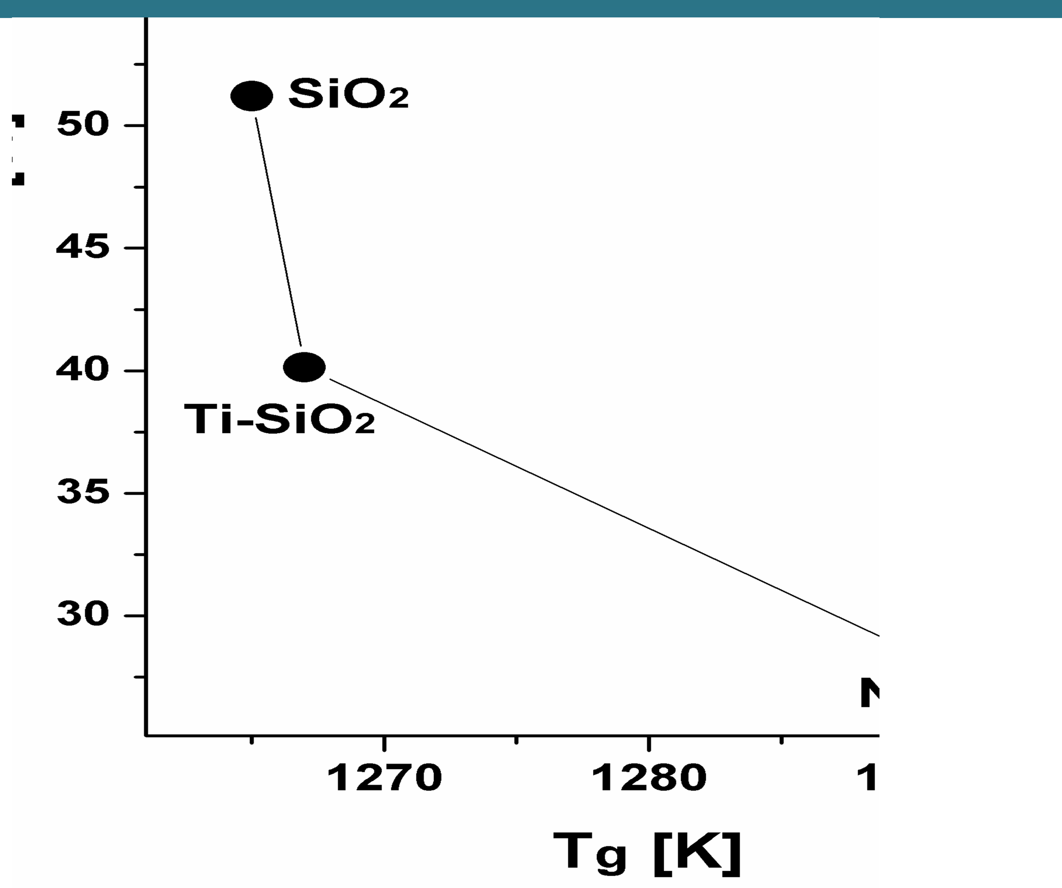


Figure 6. Surface area loss percentage due to hydrothermal treatment vs $T_g$.

## 4. Conclusions

These data indicate that Ti(IV), Zr(IV), and Nb(V) ions act as network formers: they increase $T_g$ and steam-resistance of porous silica structure, by enhancing its network connectivity. This work points at calorimetric analysis as a powerful tool for investigating structure and stability of unsupported membranes, and hence for developing basic knowledge for the effective design of steam-stabile silica membranes.

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**References:**
1) V. Boffa, 2012, Fabrication of ultramicroporous silica membranes for pervaporation and gas-separation, in Molecules at Work (B. Pignataro ed.) Wiley-VCH, 177-205.
2) V. Boffa et al. 2013, Toward the effective design of steam-stable silica-based membranes, *Microporous Mesoporous Mater.* , 179, 242–249.