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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**.

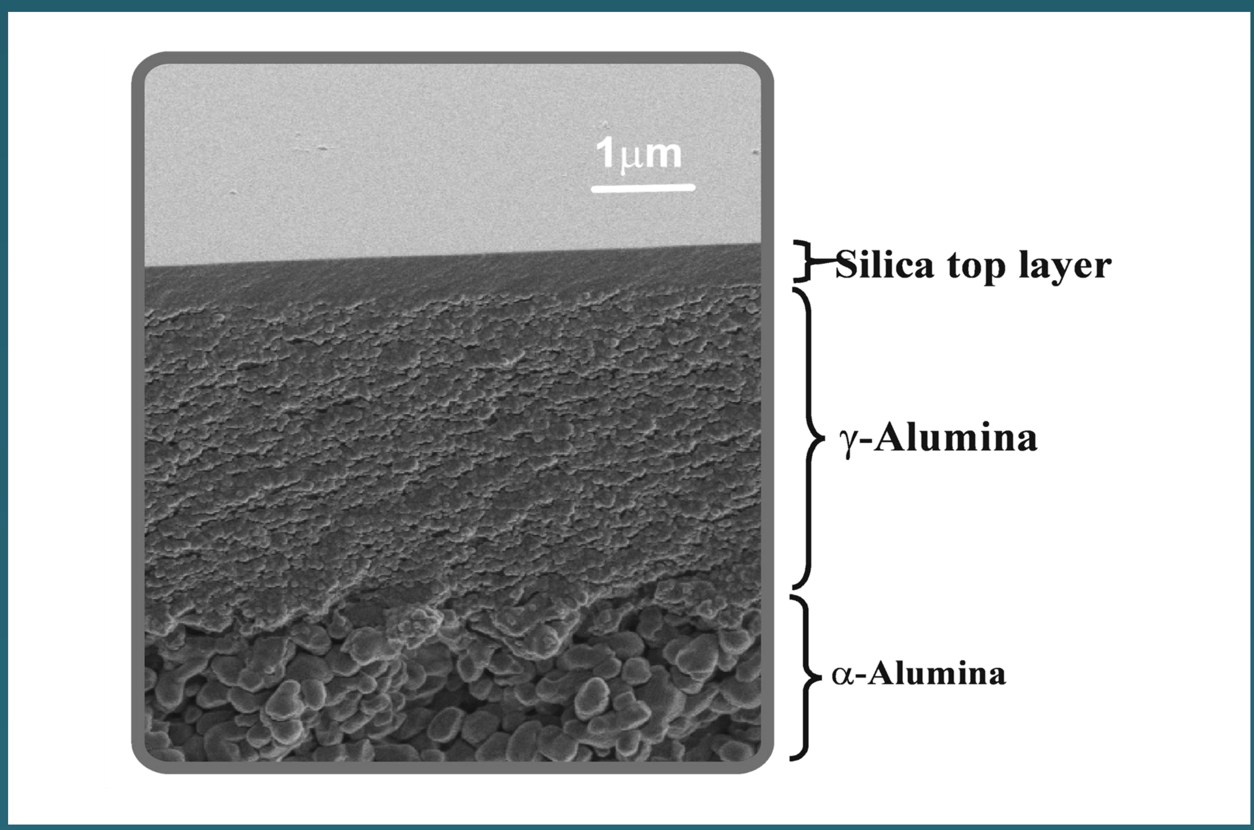

Figure 1. SEM picture of a H_2-selective silica membrane.

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.

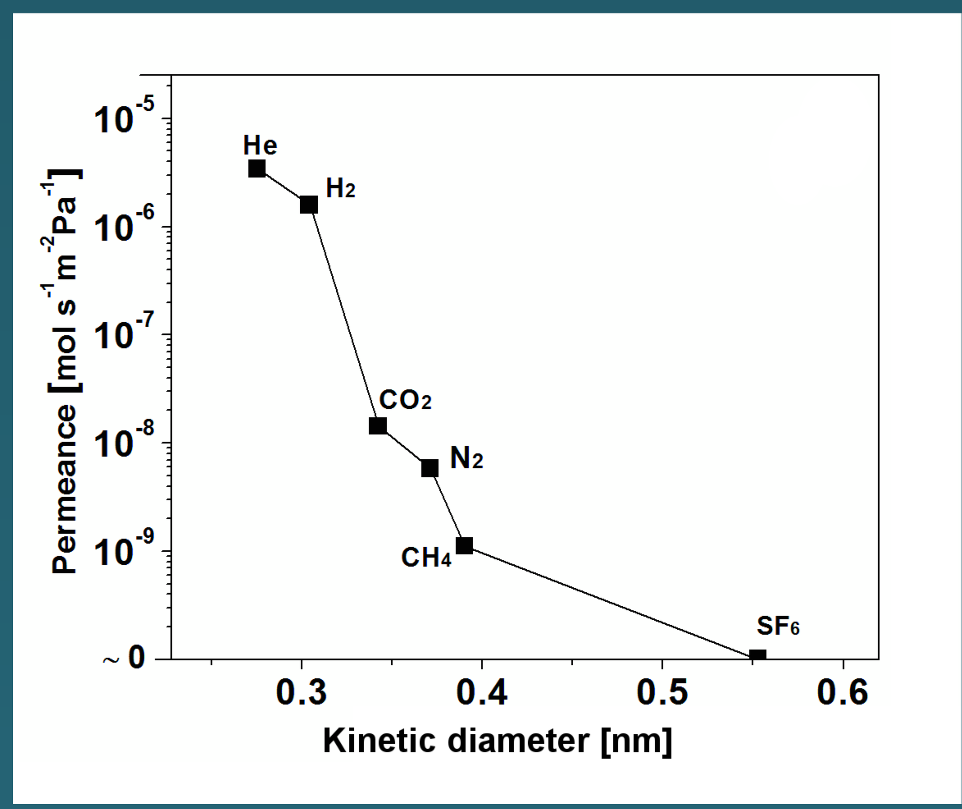

Figure 2. Permeance values of various gases through a silica membrane.

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.

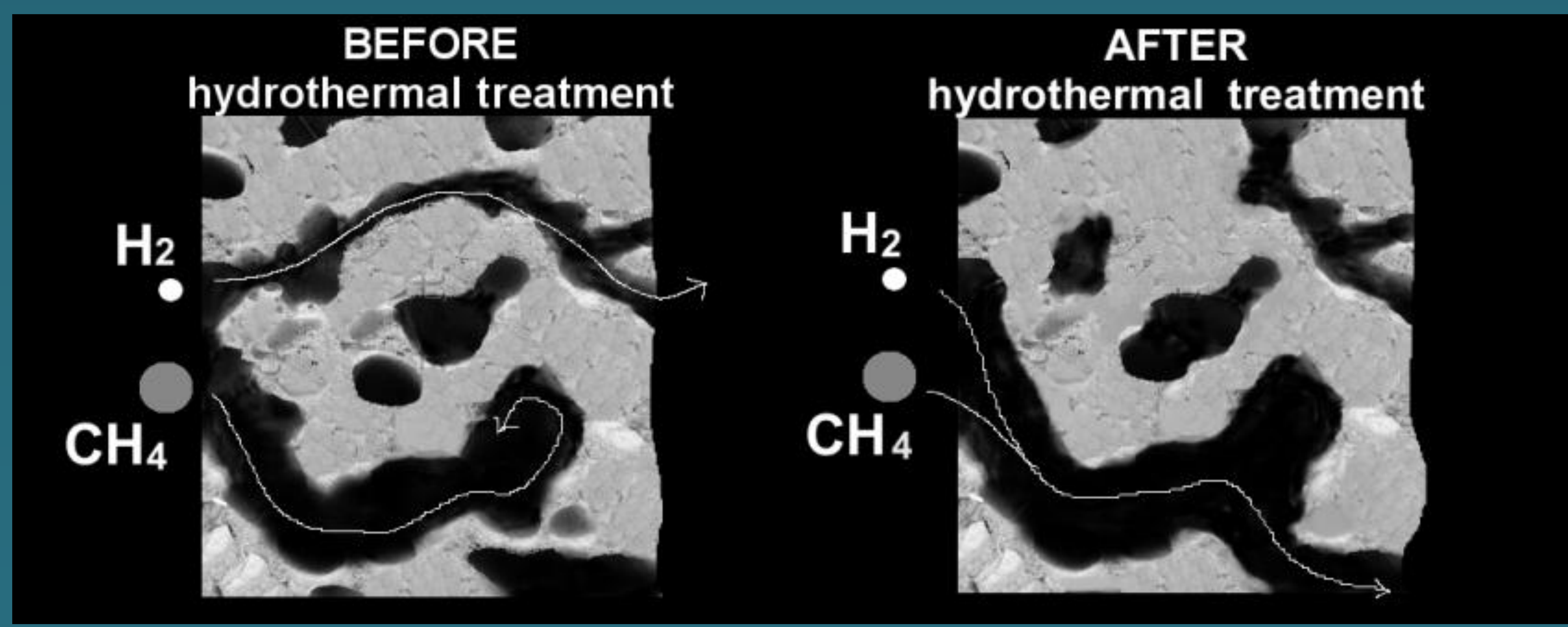

Figure 3. Representation of the structural changes in a silica membrane due to hydrothermal exposure.

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.

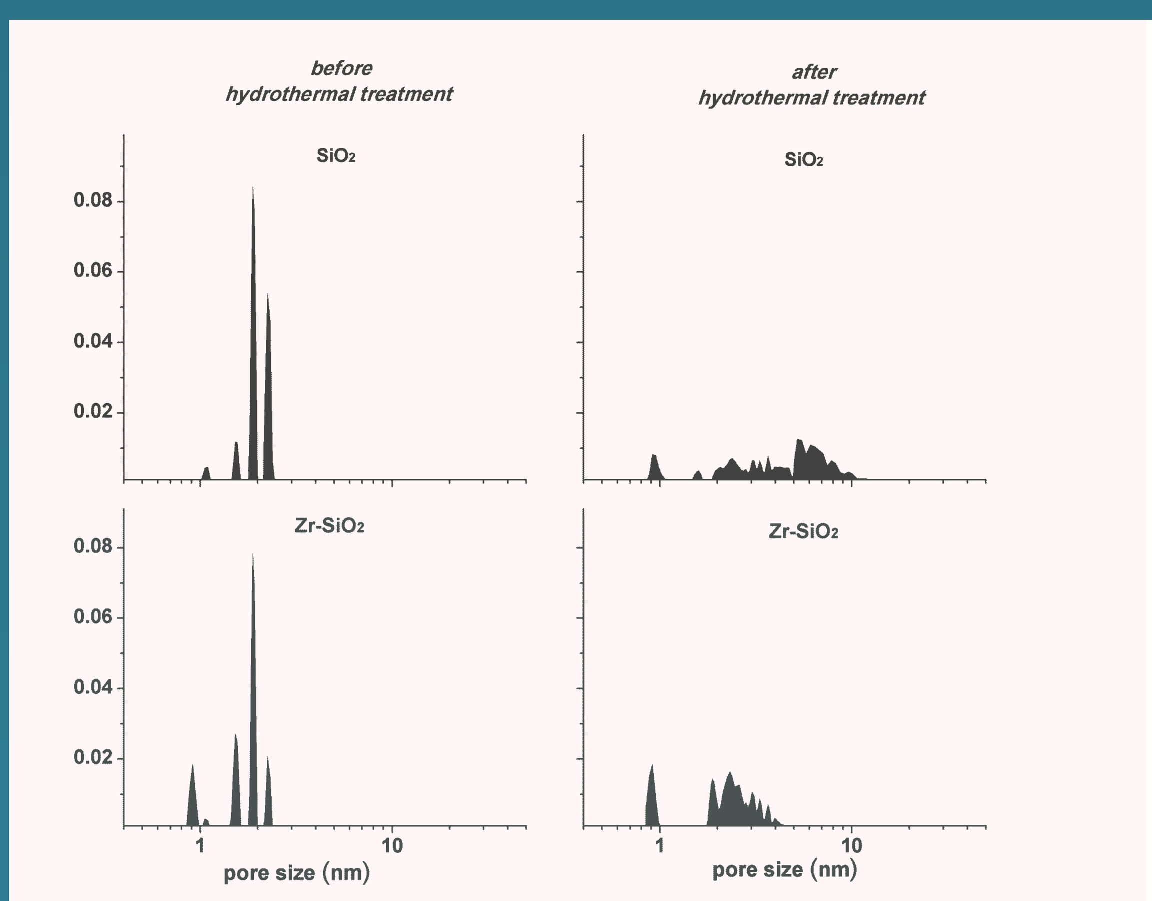

Figure 4. Pore size distributions of a pure silica and of a 5% ZrO_2- doped silica membrane before and after hydrothermal treatment.

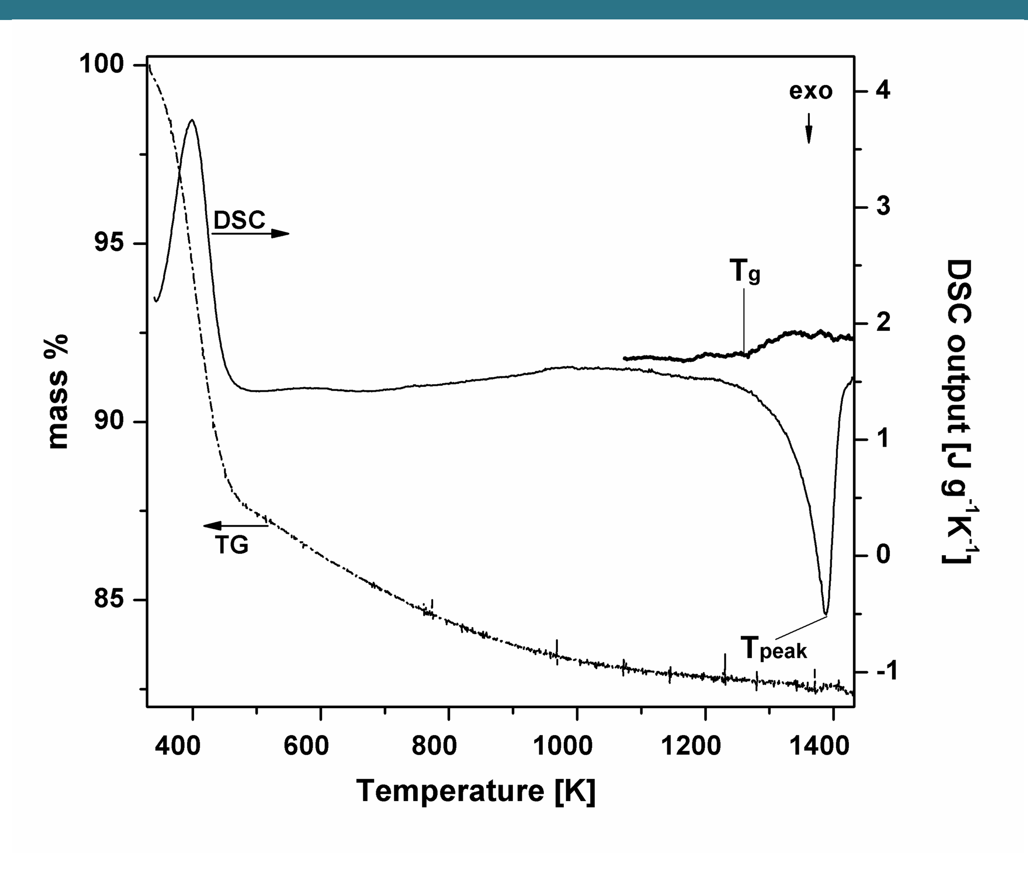

Figure 5. TGA (dashed line) and DSC (solid lines) of an unsupported membrane after calcination at 723 K for 18 h (thin lines) and at 1373 K for 24 h (thick line).

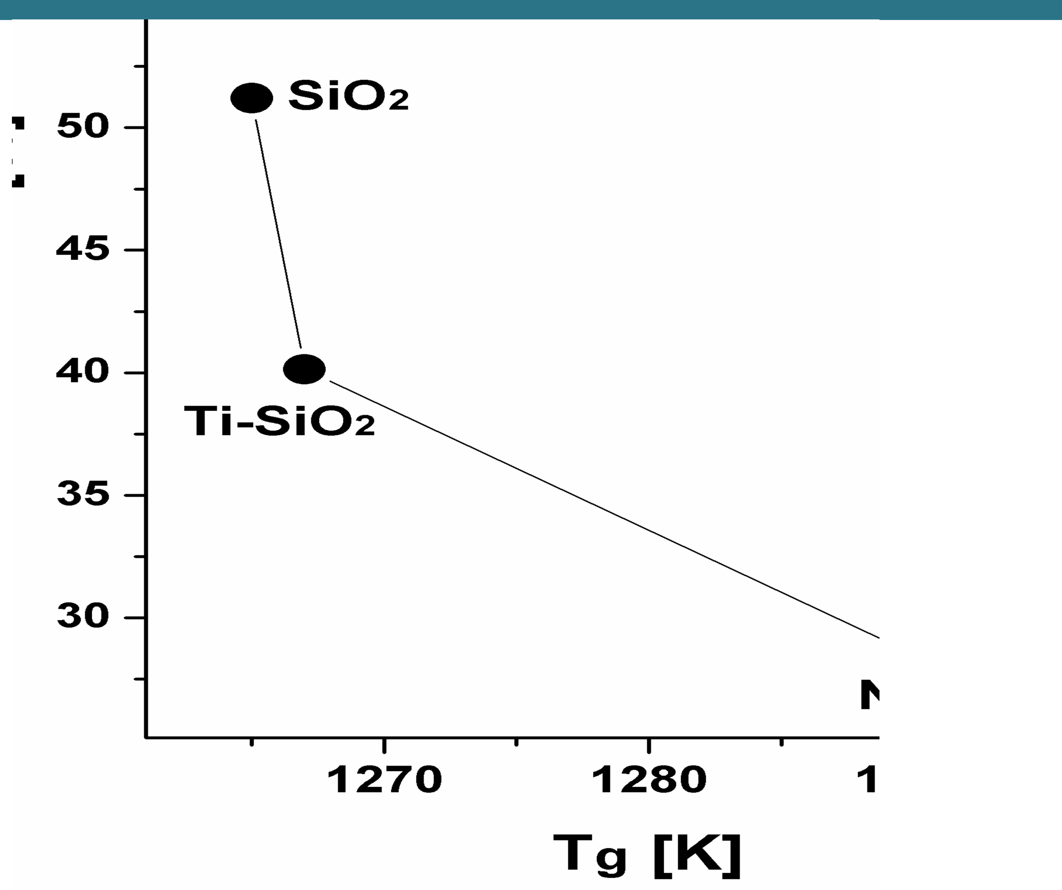

Figure 6. Surface area loss percentage due to hydrothermal treatment vs T_g.

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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