



AALBORG UNIVERSITY
DENMARK

Aalborg Universitet

Nanoporous silica membranes with high hydrothermal stability

Boffa, Vittorio; Magnacca, Gialiana; Yue, Yuanzheng

Publication date:
2012

Document Version
Early version, also known as pre-print

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Boffa, V., Magnacca, G., & Yue, Y. (2012). *Nanoporous silica membranes with high hydrothermal stability*. Poster presented at Nordic Conference on Ceramic and Glass Technology, Roskilde, Denmark.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal -

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.

Towards hydrothermally stable silica membranes

Vittorio Boffa,^{1*} Giuliana Magnacca² and Yuanzheng Yue¹

¹Chemistry Section, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University;

¹Department of Chemistry, Turin university.

vb@bio.aau.dk

Background

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

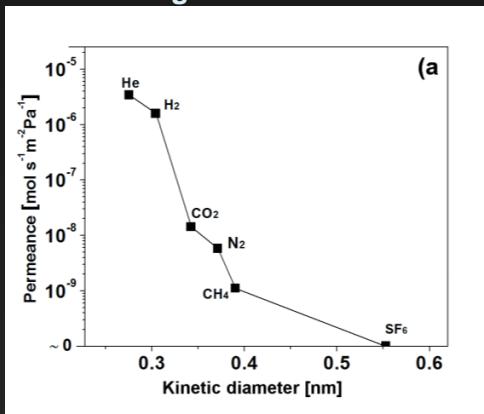


Figure 2. Permeance values of various gases through a silica membrane.

This type of membrane allow to separate the small hydrogen molecules from larger molecular species, as CO₂ and CH₄ (Figure 2). Therefore these devices appear to be promising separation systems for the upcoming technology platforms for green fuel production.

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

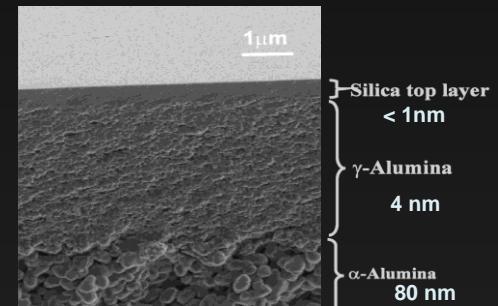


Figure 1. SEM picture of a nanoporous silica membrane.

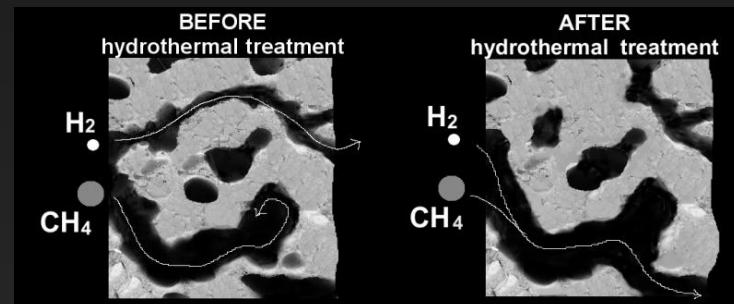


Figure 3. Representation of the structural changes produced in ultramicroporous silica during hydrothermal exposure.

Objective

Hydrothermal stability of silica membranes can be effectively improved by doping with various transition metal ions. However the impact of dopant type and concentration on the structure, stability and permeability of silica-based membranes is not clear yet, and the development of these membranes is mainly attained by an empirical approach.

In this study, surfactant micelles were used as templates to tailor 1-2 nm pores in sol-gel derived silica-based materials. Despite such pores are larger than those of hydrogen-selective membranes, this approach allowed comparing materials with different composition, but similar pore structure. Doped and undoped powders were characterized before and after hydrothermal exposure.

Results

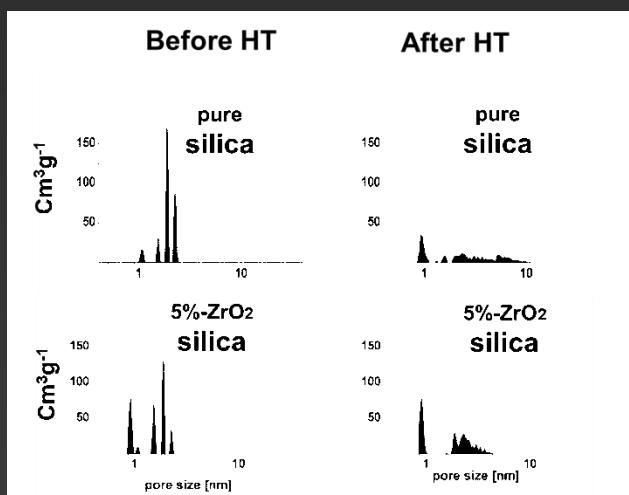


Figure 4. Pore size distributions of a pure silica membrane and of a ZrO₂-doped silica membrane before and after hydrothermal treatment.

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. These results indicate that dopants acted as network formers. Thus, the higher glass transition temperature and the enhanced hydrothermally stability of doped sample can be considered as a result of the higher network connectivity.

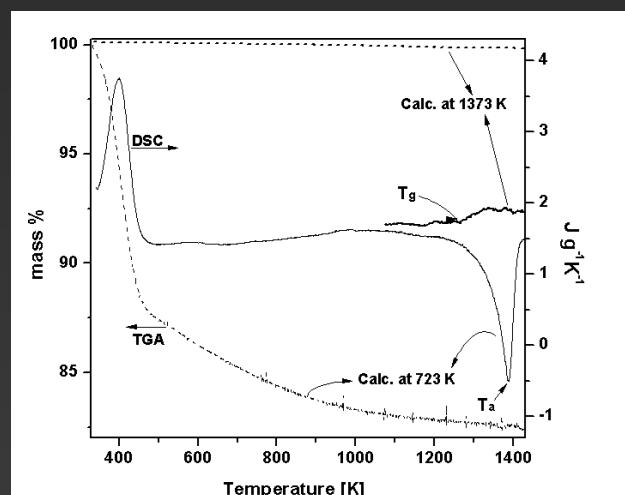


Figure 5. TGA (dashed lines) and DSC (solid lines) of an unsupported membrane after calcination at 723 K for 18 h (thin lines) and at 1373 K for 24 h (thick lines).

After hydrothermal exposure, the unsupported membranes presented lower pore volume, lower surface area and broader pore size distribution. This structural modification was more pronounced for the pure silica membranes than for the doped materials (Figure 4).

The gel-to-glass transition (T_a) and the glass transition (T_g) temperature were determined by calorimetric analysis (Figure 5).

Conclusions

This work provide bases for the effective design of highly stable silica membranes.

Acknowledgments: this work was done in the frame of the project “Low-Energy, High-Stability, Ceramic Reverse Osmosis Nano Membrane sponsored by The Danish National Advanced Technology Foundation.

Reference: V. Boffa, 2012, Fabrication of ultramicroporous silica membranes for pervaporation and gas-separation, in Molecules at Work (B. Pignataro ed.) Wiley-VCH, 177-205.

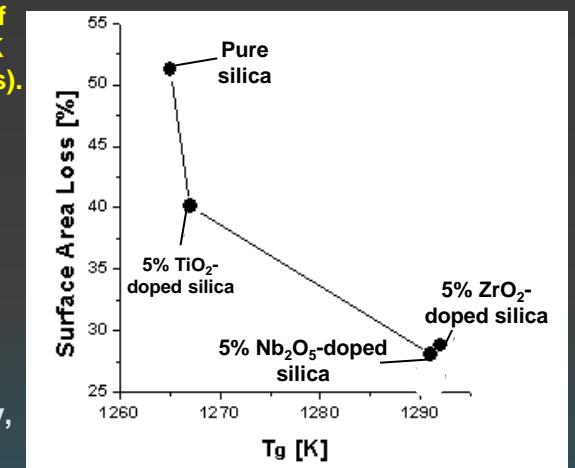


Figure 6. Surface area loss percentage due to hydrothermal treatment vs T_g.