Designing hydrothermally stable silica membranes

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1. H₂-selective silica membranes

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

These membranes allow separating the small hydrogen molecules from larger molecular species, as CO₂ and CH₄ (Figure 2). Therefore, these devices appear to be promising for the future hydrogen-based economy.

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.

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. Density was less pronounced for the doped membranes than for the pure silica reference sample (Figure 4). The gel-to-glass transition (Tgss) and the glass transition (Tg) 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.

4. Conclusions

These data indicate that Ti(IV), Zr(IV), and Nb(V) ions act as network formers: they increase Tg 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-stable 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.