

Supplementary material

*Catalyst generation*¹

Na₂WO₄·2H₂O (62.5 g, 0.19 mol) was dissolved in water (175 mL) at 85 °C. At this temperature, aqueous 37 % HCl (13.3 mL, 0.16 mol) was added. The yellow solid that was formed dissolved almost immediately, and the reaction mixture was heated to 95 °C. A solution of ZnCl₂ (6.81 g, 50 mmol) in water (75 mL) was added drop wise in 4 hours to the well-stirred solution. The slightly turbid mixture was added to a solution of Aliquat 336 (40 g, 0.10 mol) in toluene, and the mixture was stirred for 6 hours. The layers were separated and the aqueous layer was washed with pure toluene. The combined toluene layers were dried on Na₂SO₄ and the Zn-content was measured by ICP-AES (see below). A POM-concentration of 6.4 mM Q₁₂POM in toluene was calculated.

Retention measurements of Q₁₂POM stock solution

| | Pressure (bar) | Zn | | W | | Retention based on | |
|-------------------|----------------|------|-------|------|-------|--------------------|--------|
| | | g/kg | mg/kg | g/kg | mg/kg | Zn | W |
| Starting solution | | 0.21 | | 1.42 | | - | - |
| Sample 1 | 5.4 | | 0.12 | | 1.5 | >99.9% | 99.9% |
| Sample 2 | 8.9 | | 0.09 | | 0.4 | >99.9% | >99.9% |
| Sample 3 | 10.5 | | 0.05 | | 2.1 | >99.9% | 99.9% |
| Sample 4 | 11.2 | | 0.05 | | 2.3 | >99.9% | 99.8% |
| Sample 5 | 12.9 | | 0.03 | | 3.8 | >99.9% | 99.7% |
| Retentate | | 0.23 | | 1.57 | | - | - |

Q₁₂POM recycling

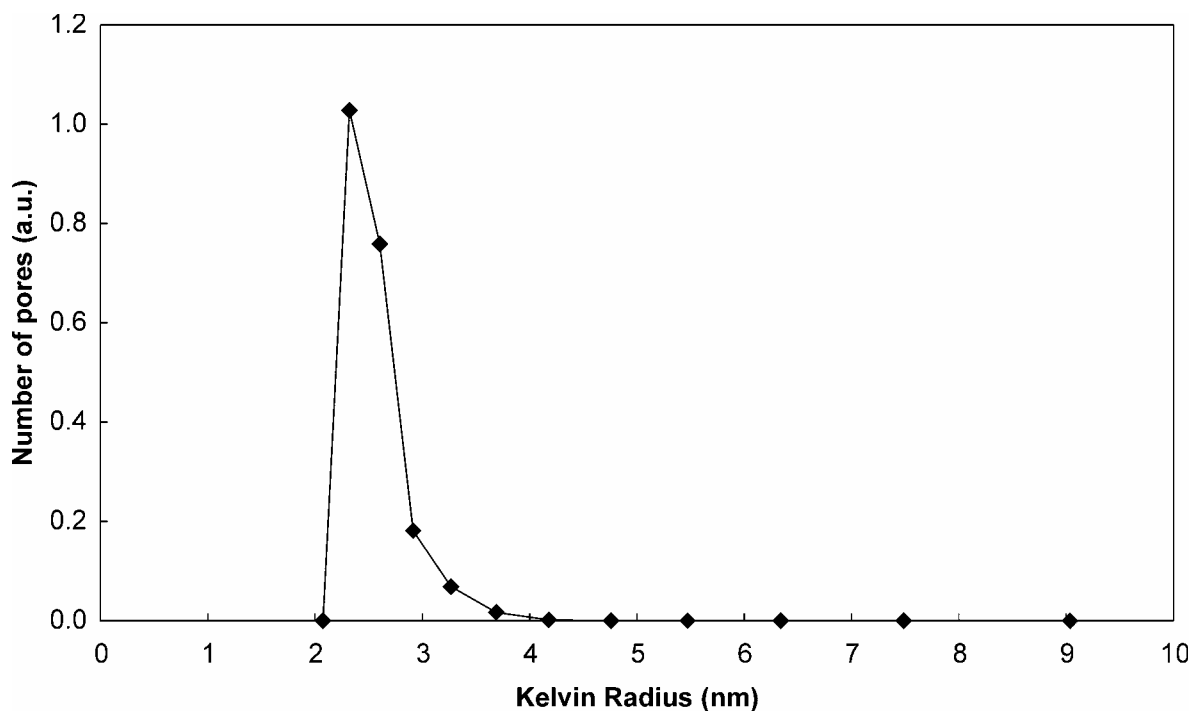
| | Amount permeate g | Zn | | Retention based on | |
|------------|-------------------|-------|-------|--------------------|-------|
| | | mg/kg | mg/kg | Zn | W |
| Permeate 1 | 9.04 | 0.5 | 272 | >99.9% | 97.8% |
| Permeate 2 | 8.14 | <0.2 | 133 | >99.9% | 99.0% |
| Permeate 3 | 10.75 | 13 | 685 | 98.6% | 93.4% |
| Permeate 4 | 10.54 | 0.8 | 335 | >99.9% | 96.9% |
| Permeate 5 | 10.68 | 0.3 | 143 | >99.9% | 98.7% |

Membrane preparation

The γ -alumina membrane consists of a macroporous α -alumina support and a thin mesoporous γ -alumina layer. The α -alumina supports were made by colloidal filtration of well-dispersed 0.4 μm α -alumina particles (AKP-30, Sumitomo). The dispersion was stabilized by peptizing with nitric acid. After drying at room temperature, the filter compact was sintered at 1100°C. Flat disks of \varnothing 39 mm and 2.0 mm thickness were obtained after machining and polishing. The final porosity of these supports is \sim 30% and the average pore size is in the range of 80-120 nm. Mesoporous γ -alumina membranes of \sim 3 mm thickness were prepared by dip-coating twice the above-mentioned porous α -alumina supports in a boehmite sol, followed by drying and calcining at 600°C for 1 h (heating/cooling rates 0.5°C/min)

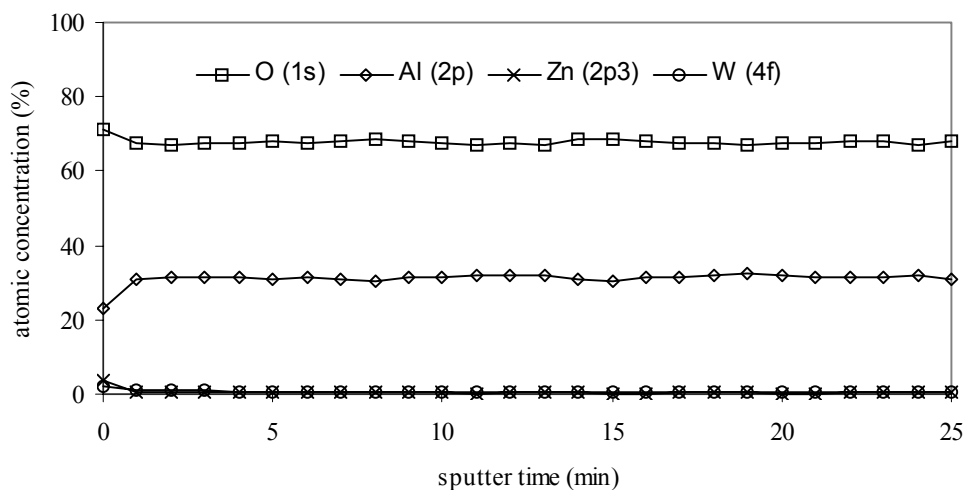
Membrane analysis

The γ -alumina membrane was characterized by permoporometry.² The pore size (d , in nm) is defined by $d = 2 \cdot (r_K + t)$, where r_K is the Kelvin radius, and t the layer thickness of the t -layer (\sim 0.3 nm).



XPS measurements

X-ray Photoelectron Spectroscopy (PHI Quantera Scanning ESCA Microprobe, USA) with Ar⁺ sputtering was carried out to identify the atomic concentrations of O, Al, Zn, and W by measuring the O 1s, Al 2p, Zn 2p3, and W 4f spectra as a function of depth inside the layer at a sputter rate of 17.9 nm/min.



| Sputter time (minutes) | O 1s | Al 2p | Zn 2p3 | W 4f |
|------------------------|-------|-------|--------|------|
| 0 | 71,39 | 22,93 | 3,69 | 1,98 |
| 1 | 67,79 | 30,75 | 0,28 | 1,17 |
| Average of 2-25 | 67,67 | 31,38 | 0,31 | 0,64 |

References:

- 1 C.M. Tourné, G.F. Tourné and F. Zonnevjlle, *J. Chem. Soc. Dalton Trans.*, 1991, 431.
- 2 N. Benes, A. Nijmeijer and H. Verweij, *Mesoporous silica membranes*, in: N.K. Kanellopoulos, ed., *Recent Advances in Gas Separation by Microporous Ceramic Membranes*, Elsevier, Amsterdam, 2000.