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Surfactant functionalised cobalt silica membranes – Gas permeation and thin film positron annihilation lifetime spectroscopy characterization

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Abstract

Gas separation is a major chemical engineering process, important to a wide variety of industries, where removal or concentration of products is desirable. As many industrial gases are generated at high temperatures and high pressures, the use of inorganic membranes, which are chemically and thermally stable, is attractive. Particularly, cobalt oxide silica membranes have been scaled up with proven performance for 2000 h operation and reaching very high H_2/CO_2 permselectivities of 500 [1]. Embedding cobalt oxide within silica films conferred functionalities otherwise not available in pure silica membranes, such as improvements for wet gas separation [2]. Although there is not a clear explanation about cobalt as functional agent, it has been stated that an increased hydrothermal stability is promoted by the coordination between high valence cobalt and silicon (Co^{3+} - Si) rather than Co^{2+} [3]. In addition, Olguin and co-workers [4] reported that the oxidation state of cobalt within silica matrix could be tailored by the halide functionality of surfactants. Although the improved understanding, the published works on the effect of surfactants on CoSi has been limited to xerogel studies, whilst membranes have yet to be fully reported. A promissory characterization technique to study thin films in membranes is positron annihilation spectroscopy (PALS) that has been reported for polymeric membranes, and crystalline inorganic (i.e., zeolite) membrane [5].

Therefore, this work investigates the use of positron annihilation lifetime spectroscopy (PALS) for the in-situ structural characterization of silica derived thin film membranes. This characterization is then correlated with the performance of surfactant functionalised CoSi membranes for gas separation. Hexyl trimethyl ammonium bromide (HTAB) was chosen as the functional surfactant in view of its effect in the oxidation state of Co. A series of membranes were prepared via a sol-gel synthesis method where the surfactant/cobalt (X) molar ratio was varied from 0 to 3. Alumina supports were coated with four layers of cationic HTBA surfactant cobalt silica sols a then calcined at 600 ºC. Single gas permeation of He, H_2, N_2 and CO_2 was performed for each membrane at different testing temperatures in the range 200–500 ◦C. The PALS experiments were performed at the mono-energetic positron source (MePS) beamline, which is one of the end stations of the radiation source ELBE (Electron Linac for beams with high Brilliance and low Emittance) at HZDR (Germany).

By using a quantified maximum entropy method, PALS allowed for the measurement of a pore size distribution (PSD) depth profile (Z at figure 1). Results showed that the coated layers adjacent to the porous alumina substrate were characterized by micropores and broad mesopores, a clear indication that the porosity of the substrate affected the pore size at the substrate and thin film interface. The last coated layer resulted in a high concentration of ultra-micropores as depicted in figure 1 (dp < 6 Å). This was attributed to the surface smoothness conferred by three previous coated layers. Surfactant incorporation from X = 0 to 1 barely alters the PSD showing high proportion of ultra-micropores at the top layer, while higher load (X = 3) promotes mesoporosity. In line with this, higher surfactant loadings resulted in an increase in gas permeation and reduction of He/CO_2 permselectivity from 91.5 to 3.8. A strong correlation with R^2 up to 0.999 was found between the ultra-micropores in the top layer and gas permselectivity (figure 2), a clear indication

that gas separation is controlled by small pore sizes. In this work, PALS showed to be a powerful tool for the characterization of the structural features of thin films.

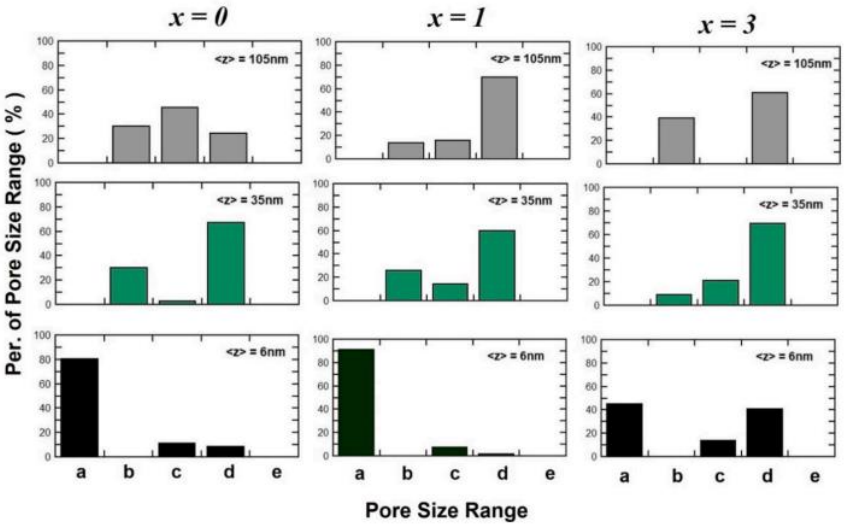

Figure 1: Pore size range Histograms in the micropore range a) dp < 6 Å, b) 6 ≤ dp ≤ 10 Å, c) 10 < dp < 20 Å, and mesopore range d) 20 ≤ dp ≤ 100 Å, e) dp > 100 Å for membranes x = 0, 1 and 3 for different implantation depths (Z).

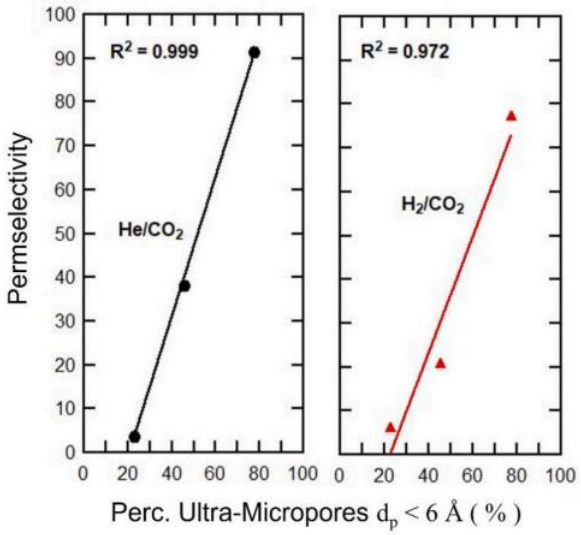

Figure 2: Percentage (%) of ultra-micropores (dp < 6 Å) over the total pore size range for the top layers based on implantation depths (<z ≥ 8 and 16 nm) PALS measurements

References

[1] C. Yacou, S. Smart, J.C. Diniz da Costa, Long term performance of a multi-tube cobalt oxide silica membrane at high temperatures for gas separation, Energy Environ. Sci. 5 (2012) 5820–5832

[2] D. Uhlmann, S. Smart, J.C. Diniz da Costa, High temperature steam investigation of cobalt oxide silica membranes for gas separation, Separ. Purif. Technol. 76 (2010) 171–178

[3] L. Liu, D.K. Wang, D.L. Martens, S. Smart, J.C. Diniz da Costa, Influence of the cobalt phase sol-gel conditioning on the hydrothermal stability of cobalt doped silica membranes, J. Membr. Sci. 475 (2015) 425–432

[4] G. Olguin, C. Yacou, S. Smart, J.C. Diniz da Costa, Tailoring the oxidation state of cobalt through halide functionality in sol-gel silica, Sci. Rep. 3 (2013) 2449, https://doi.org/10.1038/srep02449

[5] S.K. Sharma, P. Maheshwari, D. Dutta, K. Sudarshan, P.K. Pujari, Modification of microstructure of the surface and the bulk in ion-irradiated membrane studied using positron annihilation spectroscopy, Radiat. Phys. Chem. 79 (2010) 1115–1119.