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Comparison of SiO_2-ZrO_2-50% and commercial SiO_2 membranes on the pervaporative dehydration of organic solvents

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Abstract

In this work several SiO_2-ZrO_2-50% tubular pervaporation (PV) membranes were prepared by the sol–gel and hot coating method. Their PV performance was investigated regarding the separation of water/isopropanol and water/acetone mixtures in terms of water flux and selectivity. The behaviour of these membranes was compared to the performance of two commercially available silica membranes (Pervatech BV, The Netherlands, and Pervap SMS, Sulzer, Germany) on the PV of water/isopropanol mixtures and a residual water/acetone mixture coming from the manufacture process of rubber antioxidants. An exponential dependence of the water flux with respect to the water activity in the feed was confirmed for both types of membranes. The value of the mass transfer parameter that describes the interaction of the permeating component, i.e. water, with the membrane has a very similar value for the commercial silica membranes and the prepared silica–zirconia membranes.

Keywords: Pervaporation; Ceramic membranes; Silica; Zirconia

1. Introduction

Organic solvents are very common in chemical industries and their purification and recycling is conventionally carried out by energy-intensive processes, such as distillation. Pervaporation (PV) is an alternative to distillation for separating azeotropic or close-boiling component mixtures. Some inorganic membranes, based on hydrophilic zeolite and amorphous silica layers, have become commercially available in recent years [1–3].

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However, silica membranes show a questionable chemical stability when they are put in contact with hot aqueous mixtures [4]. They change their functional characteristics in the presence of humid atmosphere or water vapour [5,6]. Various techniques are being developed in order to improve the separation performance of existing microporous ceramic membranes. One of these techniques consists in doping with other oxides [7]. In this work, SiO_2-ZrO_2-50% membranes were prepared in the laboratory by the sol–gel and hot coating method and their performance in PV of isopropanol/water and acetone-water was evaluated. For comparison purposes, the performance of two commercially available silica membranes supplied by Pervatech BV (The Netherlands) and Sulzer Chemtech GmbH (Germany) is also shown in this study.

2. Experimental

SiO_2-ZrO_2-50% membranes were prepared in the laboratory of the University of Hiroshima by the sol–gel method, which comprises the sol preparation and the sol coating on a porous substrate. Several colloidal sols had been prepared with tetra-ethoxy silane and zirconium tetra-*n*-butoxide as precursors, controlling the concentration (2.0, 1.5, 1.0, 0.8, 0.5 wt% alkoxides) by adding water and acid. One month after the sol preparation, sols were coated on a commercial tubular support made of alumina, kept at 180°C while contacting quickly a cloth wetted in the sol, and burnt at 450°C for 10–20 min. This operation was repeated several times with sols of decreasing particle size, i.e. wt% alkoxides, in order to obtain the membranes that have been tested in this work. The thickness and homogeneity of the coated layer was observed on the SEM photographs taken for a membrane sample prepared by the same method. The mean pore diameters measured with the permporometry technique [8] were less than 1 nm. The separation performance of these membranes was tested in the bench-scale plant at the laboratory of the University of Hiroshima on the dehydration of synthetic mixtures of water/IPA at 75°C and water/acetone at 55°C.

Two commercially available silica membranes were also characterised and the results were detailed in previous works [1,9]. These membranes were manufactured by Pervatech BV (Pervatech PVP, The Netherlands) and Sulzer Chemtech GmbH (Sulzer SMS, Germany), respectively. Both consist of an amorphous silica top layer over a tubular composite alumina porous support. In these cases, PV experiments were run in a specially built stainless steel bench-scale pilot plant at the University of Cantabria, using synthetic water/isopropanol mixtures and an industrial water/acetone waste effluent containing about 25 wt% water in acetone coming from the chemical production of rubber antioxidants. Water/isopropanol dehydration experiments shown in this study were performed at 70°C and water/acetone experiments at 50°C, that is, below their normal boiling points.

3. Results and discussion

The structural characteristics of the SiO_2-ZrO_2-50% membranes are shown in Fig. 1. The microporous silica–zirconia layer obtained had a thickness of about 0.5 μm, as it is observed in Fig. 1a for a membrane sample. Fig. 1b shows the observed pore size distributions of yet another membrane sample prepared by the same sol–gel and hot coating after coating sols of decreasing particle size. The average pore size is lower as the particle size of the last sol coated is also lower.

Fig. 2a shows the water flux as a function of water content in the feed for the SiO_2-ZrO_2-50% membranes during PV experiments of water/IPA at 75ºC and Fig. 2b — the water flux as a function of water content for the PV experiments of water/acetone at 55ºC. The results obtained using the commercial silica membranes were included for comparison. It may be observed that SiO_2-ZrO_2-50% membranes give a higher water flux similar