Can inorganic membranes compete with organic ones?
Perovskite hollow fibres for O\textsubscript{2-}separation and supported H\textsubscript{2}-selective zeolite membranes

Jürgen Caro\textsuperscript{a*}, Thomas Schiestel\textsuperscript{b}, Steffen Werth\textsuperscript{c}, Haihui Wang\textsuperscript{a}, Manfred Noack\textsuperscript{d}

\textsuperscript{a}Institute for Physical Chemistry, University of Hannover, Callinstr. 3-3A, D-30167 Hannover, Germany

\textsuperscript{b}Fraunhofer Institute of Interfacial Engineering and Biotechnology (IGB), Nobelstr. 12, D-70569 Stuttgart, Germany

\textsuperscript{c}Uhde GmbH, Friedrich-Uhde-Str. 15, D-44141 Dortmund, Germany

\textsuperscript{d}Leibniz-Institute for Catalysis (former ACA) Berlin-Adlershof, R-Willstätter-Str. 12, D-12489 Berlin, Germany

Received 25 October 2005; accepted 6 March 2006

Abstract

So far, large scale industrial separations with inorganic membranes and catalytic membrane reactors in process intensification do not exist. Two prominent developments which are near to a commercialization are discussed: perovskite membranes for oxygen separation and zeolite membranes for molecular sieving.

Keywords: Inorganic membranes; Perovskite; Oxygen separation; Zeolite membrane; Molecular sieving

1. Introduction

Polymer membranes have become a valuable tool in dialysis, natural gas treatment and refinery gas processing. So far, no large-scale industrial applications of inorganic membranes are known. However, there are world wide intense R&D activities in developing (i) perovskite membranes and (ii) shape-selective zeolite membranes. The basic concepts for the development of these novel inorganic membranes and modules were adopted from the experience obtained by preparing organic membranes and modules: spinning of hollow fibres and supported thin separation layers.

2. Experimental

The calcined Ba(Co,Fe,Zr)O\textsubscript{3-δ} powder was spun into fibres at the Fraunhofer Institute for Interfacial Engineering and Biotechnology (IGB)
by phase inversion spinning (see [1,2]). A homogeneous slurry of a polymer solution and the Ba(Co,Fe,Zr)O$_{3\delta}$ powder was obtained by ball milling up to 24 h. The slurry was spun through a spinneret and the obtained infinite green fibre was cut into 0.5 m long pieces before sintering the hollow fibres at $T > 1200^\circ$C in a hanging position (Fig. 1).

The zeolite membranes (Fig. 2) were prepared at the ACA [3] by using ex situ synthesized silicalite I seeds. In the alkaline pH-range, the negatively charged silicalite I seeds attach electrostatically to the positively charged surface of the $\alpha$-alumina support (from hitk Hermsdorf, Germany). The positive surface charge of the alumina support can be increased by adsorption of positively charged polymers (poly-DAD-MAC, Redifloc). In a subsequent synthesis the seed crystals grow for 24 h at a temperature of 180$^\circ$C under hydrothermal conditions in autoclaves to a continuous molecular sieve layer. The composition of the molecular sieve synthesis solution was 100 SiO$_2$·9 TPAOH·2200 H$_2$O.

3. Results and discussion

$O_2$-enriched air can be produced by transporting oxygen from slightly pressurized air through a Ba(Co,Fe,Zr)O$_{3\delta}$ perovskite hollow fibre membrane to air of lower pressure thus increasing the oxygen content of this air to typically 40–50 vol.% $O_2$ (Fig. 3) [4]. Ba(Co,Fe,Zr)O$_{3\delta}$ hollow fibres with a wall thickness of ca. 175 $\mu$m can be used as well to produce by means of inert sweep gases pure oxygen (Fig. 4). In the example He was used as sweep. Long time permeation with steam shows that the Ba(Co,Fe,Zr)O$_{3\delta}$ fibre is stable at least for 200 h. At 500$^\circ$C the MFI silicalite I membrane shows $H_2$ selectivity of 70 at
500°C and a flux of 1 m³ (STP) H₂/m² h bar and can be used in membrane assisted dehydrogenations (Fig. 5) [5].

4. Conclusions

The spinning process adopted from preparing polymer hollow fibre membranes can be successfully applied to the manufacturing of perovskite hollow fibres with infinite O₂-selectivity, relative high fluxes and sufficient durability at 850°C. The technique of supported thin membrane films could be transferred to the crystallization of zeolite molecular sieve layers.

References