

Preparation of hollow-fibre composite carbon–zeolite membranes

S.P.J. Smith ^{a,*}, V.M. Linkov ^a, R.D. Sanderson ^a, L.F. Petrik ^b, C.T. O'Connor ^b,
K. Keiser ^c

^a *Institute for Polymer Science, University of Stellenbosch, Stellenbosch 7600, South Africa*

^b *Department of Chemical Engineering, University of Cape Town, Cape Town 8000, South Africa*

^c *Department of Chemical Engineering, University of Twente, 7500 AE Enschede, Netherlands*

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Abstract

Carbon membranes, produced by thermo-oxidative stabilization of polyacrylonitrile (PAN) precursors, were used as porous supports for continuous zeolite layers to give composite zeolite–carbon membranes. Different zeolite growth techniques were used, and the membranes were characterized by means of scanning electron microscopy (SEM), elemental dispersive X-ray analysis (EDAX) and X-ray diffraction (XRD).

Keywords: Zeolite; Carbon membranes; Hollow fibres

1. Introduction

Inorganic membranes hold great promise for various separation and catalytic processes due to their good mechanical properties and stability at high temperatures and in harsh environments. The production of these membranes is, at present, an emerging technology with many problem areas yet to be addressed; among these is the fabrication of uniform, sub 8 Å, microporous inorganic membranes. In this regard, the unique combination of properties of zeolites, such as microporosity with uniform pore dimensions, ion-exchange capacity and high thermal stability, makes them attractive candidates for introduction to the field of inorganic membranes [1]. Several types of zeolite-based membranes have already found applications and proved to be successful on laboratory scale in catalytic membrane reactors and separation pro-

cesses at elevated temperatures, e.g., ceramic and metal-based, as well as self-supported, zeolite membranes [2–8]. The main disadvantage of these systems has been that usually only flat-sheet membranes or tubes, with insufficient surface area, have been produced. One possible way to overcome this disadvantage may be by the production of composite multi-layer hollow-fibre membranes, made by coating a suitable inorganic support with a thin film of zeolite.

Hollow-fibre carbon membranes, produced by pyrolysis of cellulose precursors, were introduced in 1983 by Koresh and Soffer [9]. Because of their good gas separation properties and stability at elevated temperatures and in harsh environments, the international membrane community took an interest in this type of membrane, and, subsequently, precursor materials other than cellulose such as phenolic resins [10], pitch mesophase [11] and polyimides [12] were used. Recently, a range of flexible hollow fibre carbon membranes with

* Corresponding author.

high porosity and good mechanical properties were obtained by the carbonization of highly asymmetrical PAN precursors. These were produced by using various combinations of solvent and non-solvents as the precipitation media [13], and the resultant membranes had high gas fluxes through them. Composite ceramic-carbon hollow-fibre membranes were also produced by sol-gel deposition of metal oxides on their outer surfaces [14]. In the current study an attempt is made to prepare a composite zeolite membrane in the form of a hollow fine fibre by deposition of various zeolites onto hollow-fibre carbon membranes.

2. Experimental

The production of mesoporous hollow-fibre carbon membranes is described elsewhere [15]. Prior to the coating operation, the membranes were thoroughly washed with ethanol and acetone and dried overnight in a vacuum oven at 100°C.

The coating of the membranes was performed with three different zeolites: ZSM-5, mordenite and silicalite-1. Zeolite growing operations were performed in stainless-steel autoclaves in which samples of carbon membranes were treated with solutions containing the following components:

ZSM-5: NaOH (1.87 g, analytical grade), H₂O (100 g), tetrapropylammonium bromide (TPA-Br) (25.18 g, Merck, analytical grade), colloidal silica (31.84 g, Du Pont, AS-40), Al(OH)₃ (0.48 g, Merck, analytical grade).

Mordenite: NaOH (1.41 g, analytical grade), H₂O (101.42 g), NaAlO₂ (12.61 g, technical grade, Al₂O₃ = 56%, Na₂O = 37%), colloidal silica (104.42 g, Du Pont, AS-40).

Silicalite-1: NaOH (1.2 g, analytical grade), H₂O, tetrapropylammonium hydroxide (TPA-OH) (80 g, Merck, analytical grade), silicic acid, SiO₂·H₂O (17.4 g, analytical grade).

The individual sols were aged for 60 min at room temperature. In all cases, the hydrothermal growth was carried out over a period of three



Fig. 1. Silicalite-1 on carbon membrane.

days. The autoclave temperatures were 185°C for ZSM-5 and mordenite and 120°C for silicalite 1. On completion of the synthesis the membranes were repeatedly washed in hot water and dried overnight in a vacuum oven at 100°C.

An attempt was made to facilitate zeolite growth by modifying carbon membrane surfaces with the purpose of forming nucleation sites. Two modification methods were used. The first method involved surface oxidation, including hot air treatment (150–160°C over 2 h), and ozone treatment (25°C, 30 min), using a Fisher 503 ozone generator. The object of the second method was to impregnate the membranes' outer surfaces with silicon atoms. This included flushing of oxygenated membranes with tetraethoxysilane, followed by heat treatment in air and dipping of PAN precursors in a 1.17% silicon rubber solution for 2 h prior to carbonization.

Coated membranes were studied with a Jeol JSM-35 SEM microscope, an International 707B EDAX system and a Philips XRD instrument.

3. Results and discussion

When carbon membranes with untreated surfaces were used, only deposition experiments involving the silicalite-1 synthesis mixture resulted in the formation of a continuous zeolite layer. SEM images revealed uniform coatings of approximately 1 µm thickness, with no visible cracks or any other defects (Fig. 1). Because of the high porosity of carbon membranes it was expected that during the deposition operation, the growth of zeolites would take place not only on the surface but also inside the membrane wall. This assumption was only partially supported by the SEM

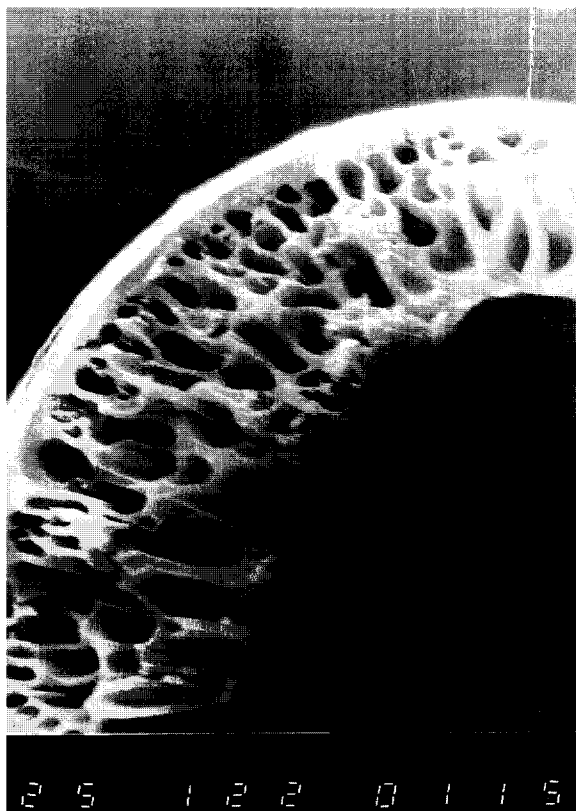


Fig. 2. Cross-section of carbon membrane.

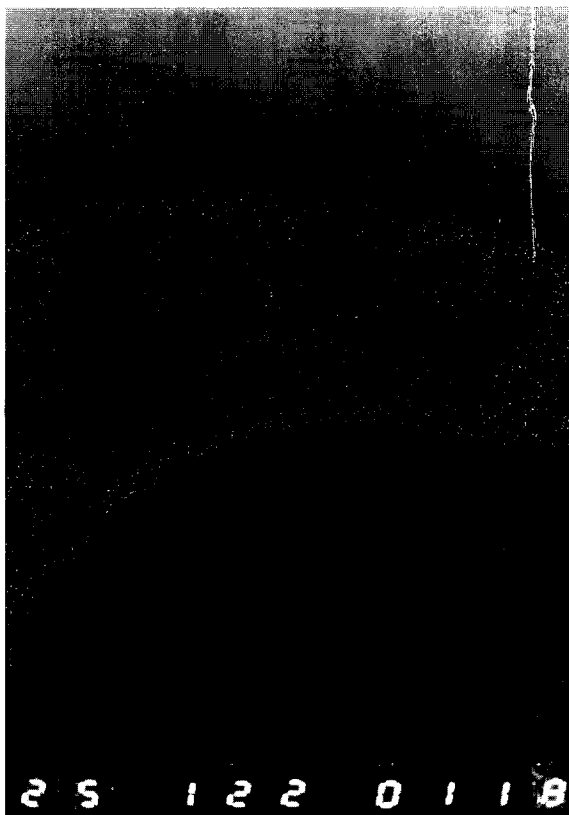


Fig. 3. EDAX element mapping.

image of the membrane's cross-section, shown in Fig. 2, and which did not appear to differ from that of an untreated carbon membrane. The inner channels were not blocked and only small crystals were attached to the walls of the voids close to the membrane lumen.

A clear picture of zeolite distribution inside the membrane wall was obtained by EDAX mapping of Si atoms (Fig. 3). Because the composite layer is very thin and due to stripping of the coating during the membrane fracturation, it was impossible to detect the zeolite surface layer by this method. It is, however, evident from the EDAX element mapping that an area with higher concentration of silicon atoms occurs at the core-side of the membrane. The reason for this is related to the asymmetrical structure of the carbon membranes. Small pores of the outer skin of the membrane may make it impossible for the zeolite synthesis solution to penetrate into the inner porous structure. Alternatively, the rough surface of the membrane lumen with micropores of several

micrometers in diameter allows absorption of large quantities of the synthesis solution with subsequent formation of large zeolite crystals.

The fact that only isolated crystals were observed on surfaces of the carbon membranes in cases of ZSM-5 and mordenite coatings was attributed to the lack of active surface sites. It was decided, therefore, to add more active sites to membrane surfaces by their chemical modification or by absorption. After the deposition experiments were carried out on modified membranes it became clear that mere surface oxidation did not significantly improve zeolite growth. On the other hand, impregnation of the membrane surfaces with silicon atoms, carried out by absorption of tetraethoxysilane with subsequent heat treatment in an oxidising atmosphere, resulted in the formation of continuous layers of both ZSM-5 and mordenite by the same deposition operation as was used for unmodified carbon membranes. The layer of densely packed crystals of approximately 11 μm thickness is clearly visible in the SEM image

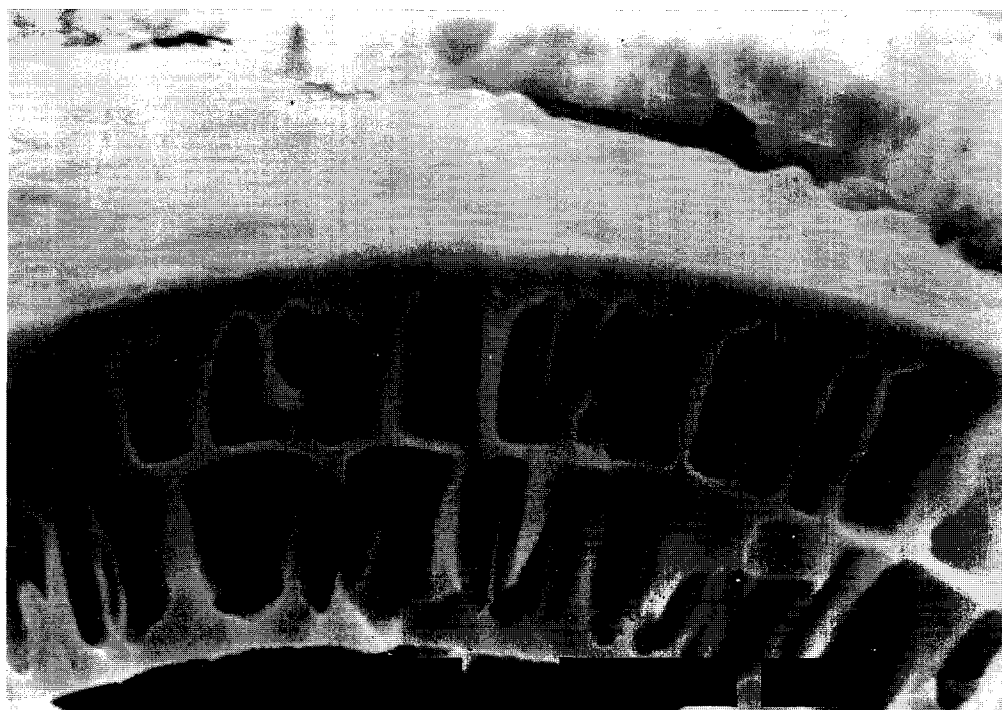


Fig. 4. ZSM-5 layer on carbon membrane.

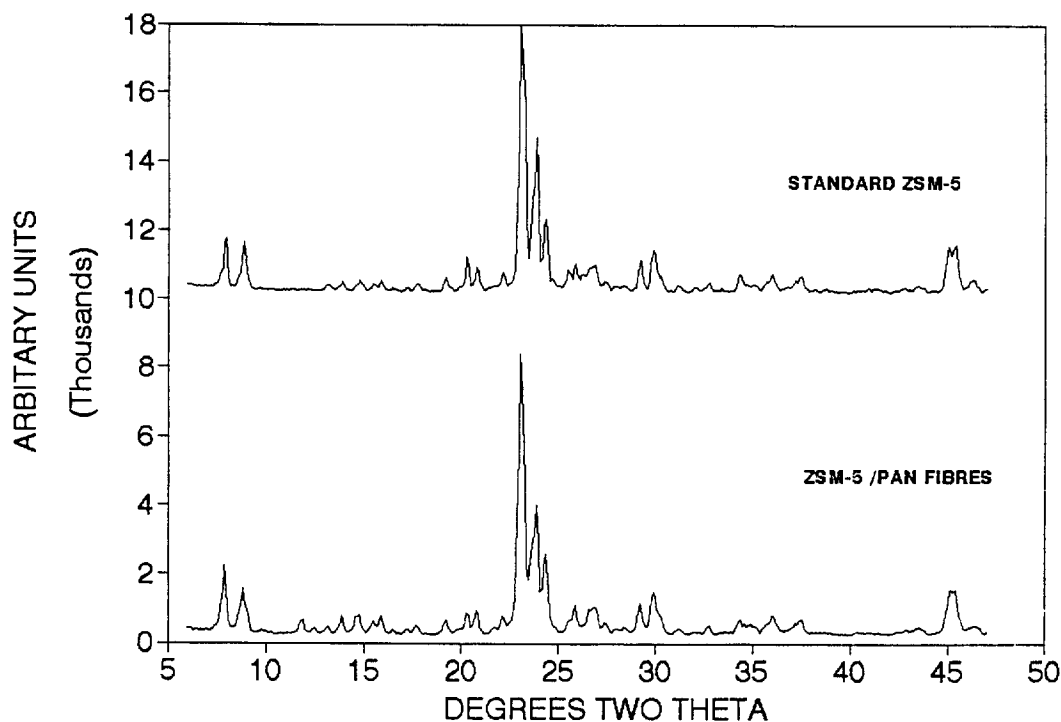


Fig. 5. XRD spectra of standard ZSM-5 compared to ZSM-5 prepared in the presence of PAN.

of the cross-section of a ZSM-5-coated membrane (Fig. 4). This modified synthesis method incorporating ZSM-5 and the carbon membranes showed no phase or crystallinity changes, according to the XRD spectra (Fig. 5). The XRD spectra were obtained from crystals scraped from the coated hollow-fibres. It is therefore presumed that ZSM-5 formation is not in any way compromised by the addition of the carbon membranes to the synthesis mixture.

4. Conclusions

The possibility of the utilisation of hollow-fibre carbon membranes as supports for continuous zeolite layers was demonstrated. The generation of the silicon-containing active sites on membrane surfaces enhanced the deposition process considerably. Research is continuing and will be focused

on gas separation studies of the zeolite-carbon composite membranes.

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