Journal of Membrane Science 524 (2017) 73–78

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

High-capacity open bore membrane chromatography column based on micro-packed ceramic hollow fibres

Melanie Lee, Bo Wang, Kang Li*

Department of Chemical Engineering, Imperial College London, SW7 2AZ, UK

ARTICLE INFO

Keywords:
Ceramic membrane
Gas chromatography
High-capacity
Hollow fibre
Packed micro-channels

ABSTRACT

Micro-structured ceramic hollow fibres as a new (GC) column configuration has been designed, fabricated, and executed for the separation of gases. The design consists of ceramic hollow fibres with intensively self-arranged open micro-channels in its wall, which act as storage space, and the stationary phase is packed inside the micro-channels. The hollow lumen leads to negligible pressure drop along the GC column that is similar to the common capillary columns, whilst the intensively distributed micro-channels provide spacious volume for packing the stationary phase to realise much enhanced capacity that is close to common packed columns. Using alumina hollow fibre as an example, this novel design has been demonstrated as a GC column packed with 5 Å molecular sieve particles and used to successfully separate nitrogen and oxygen. Such a GC column with a length of 8 m was able to separate O_2 and N_2 completely, with an injection volume of 90 μL, which is 20–30 times higher than a typical capillary column, and a negligible pressure drop of only 0.01 bar. The theoretical plate number of this column for oxygen is up to almost 30 times higher than a commercial packed column's, and for nitrogen it is almost 10 times higher.

1. Introduction

Packed and open capillary columns currently dominate the gas chromatography (GC) industry, and albeit both have their own advantages, they each have their unique shortcomings as well [1–3]. A Packed bed of adsorbents provides high available surface area and adsorption capacity but is subjected to high pressure drops; and although the coated film of catalyst/adsorbent on the inner surface gives low pressure drop, the surface area/adsorption capacity is limited (Fig. 1). Furthermore, it suffers from losing catalyst/adsorbent over time. Hence, solutions of constructing catalytic micro-reactors to overcome these shortages are needed.

Ceramic hollow fibre membranes offer high chemical, thermal and mechanical stability as well as high packing densities [4–6]. The common asymmetric ceramic hollow fibre membranes can possess intensive self-arranged micro-channels, which can potentially be used to contain a wide range of functional materials to form various functional devices [7,8]. In most of the previous literature, access to the volume of micro-channels is difficult, due to the presence of two barrier layers that sandwich them at the inner and outer surfaces [7]. However, the barrier layers can be selectively removed during the fabrication process, allowing easy access to these free spaces from either the inner or the outer surface [8–10]. So far, ceramic hollow fibre membranes with open micro-channels accessible from the lumen surface have been studied to pack catalysts to form catalytic micro-reactors, but such catalytic micro-reactors are inconvenient to assemble and the catalyst will potentially be lost with the flowing fluid.

Much research has been placed on membrane chromatography, particularly in liquid chromatography for various bioprocessing applications [11]. They possess many advantages such as low pressure drops and high mass transfer, and can achieve membrane separation and chromatography in a single step. These membranes are found in various forms, such as flat sheet and hollow fibres, and are made from organic materials in almost all cases. The material of the membrane itself is the stationary phase and is also the current drawback of this technology. Currently, the low binding capacity of the membrane materials, which determines the chromatographic capability of the system, is retarding the wide-spread use of membrane chromatography systems. The beauty of the new type of chromatography column introduced this study is its flexibility, stability, and high capacity. The most suitable adsorbent on the market can be chosen and packed into the vast amounts of micro-channels in the walls of the inorganic hollow fibre membrane, and the membrane support can be made from different inorganic or metal materials. This gives a lot of flexibility in the operating conditions that can be used, such as at very high and low temperatures, across a wide pH scale, and can be cleaned and

* Corresponding author.
E-mail address: kang.li@imperial.ac.uk (K. Li).

http://dx.doi.org/10.1016/j.memsci.2016.11.010
Received 11 September 2016; Received in revised form 31 October 2016; Accepted 2 November 2016
Available online 15 November 2016

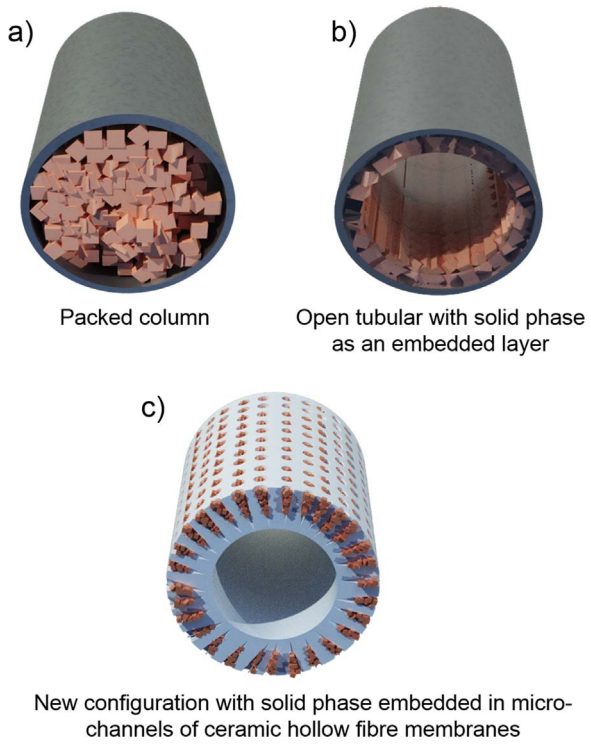

Fig. 1. Common gas chromatography configurations a, b) and the proposed new configuration using packed micro-channels in hollow fibres c).

regenerated easily.

In this study, for the first time, the application of micro-structured ceramic hollow fibre membranes for gas chromatography has been explored. We prepared alumina hollow fibre membranes by an interfacial instability-induced micro-channelling method [4], whereby micro-channels are open on the outer surface but closed on the inner surface (Fig. 1c). In this proof-of-concept study, for the first time, we test the feasibility of using alumina hollow fibres as the support for storing the stationary phase to form an open-bore gas chromatography column to separate oxygen and nitrogen in air. The 5 Å molecular sieve particles were first deposited and packed into the micro-channels using vacuum suction, and the lumen side layer acts like a membrane barrier to prevent the loss of the particles. Then, the packed hollow fibres were dried and packed into stainless steel tubing to form columns of different lengths, which were connected to a mass spectrometer to detect and analyse the composition of the column outlet.

2. Experimental

2.1. Materials and chemicals

Aluminium oxide (Al_2O_3) (alpha, 99.9% metals basis, surface area 6–8 m^2/g, mean particle size (d_{50}) 1 μm, Inframat Corporation) was used as supplied. Polyethersulfone (PESf) (Radal A300, Ameco Performance, USA) was used as the polymeric binder. Dimethyl sulphoxide (DMSO, HPLC grade, VWR), and N-methyl-2-pyrrolidone (NMP, HPLC grade, VWR) were used as solvents. Arlacel P135 (polyethylene glycol 30-dipolyhydroxystearate, Uniqema) is used as the additive. De-ionized water was used as the bore fluid and NMP was used as the outer coagulant. 5 Å molecular sieve was purchased form Sigma Aldrich, UK. The carrier gas was Argon, purchased from BOC, UK.

2.2. Fabrication of alumina hollow fibre membranes with open micro-channels

The fabrication process is based on the phase-inversion technique used to prepare the hollow fibres with open micro-channels on the outer surface. A triple-layered spinneret was used to spin a layer of ceramic fibre inside an outer layer consisting of solvent only to achieve an open structure on the outer surface. A uniform suspension composed of ceramic particles (59.9 wt%), DMSO (33.6 wt%) and polymeric binder (6.0 wt%), as well as an additive acting as a dispersant (0.5 wt%), was prepared via ball milling. The ceramic suspension was then degassed under vacuum with stirring to fully remove bubbles, and then transferred into a 200 mL stainless steel syringe controlled by a syringe pump (Harvard PHD22/200 HPsi and KDS410). NMP was then transferred into a 100 mL stainless steel syringe controlled by another syringe pump. At an air gap of 25 cm, the bore fluid, ceramic suspension and solvent were extruded through the triple-layered spinneret into the external coagulation water bath via syringe pumps with flow rates 40 mL min^{-1}, 7 mL min^{-1} and 5 mL min^{-1}, respectively. The precursor hollow fibre membranes were removed from the external coagulant bath when phase-inversion was complete, and were dried and straightened at room temperature. They were then cut into the required length for subsequent calcination and sintering. The membranes were heat treated in air (CARBOLITE furnace) and the temperature was increased from room temperature to 600 °C at a rate of 2 °C/min and held for 2 h, then to a target temperature of 1500 °C at a rate of 3 °C/min and held for 4 h, and the temperature was reduced back to room temperature at a rate of 5 °C/min.

2.3. Set up of the hollow fibre GC system

The sintered hollow fibres were then potted into ¼ inch NPT male connectors and sealed with epoxy resin. On the other hand, 5 Å molecular sieve particles were dispersed in water (1.2 g/L) under mechanical stirring. The fibre was then connected to a vacuum filtering flask connected to a vacuum pump, as shown in Fig. 2. A vacuum was applied from the lumen of the hollow fibre, which suctioned the molecular sieve particles into the micro-channels and clear water passed through the membrane and into the flask. The hollow fibres were then dried in ambient conditions. The hollow fibres were broken from the NPT male connectors and packed into 20 cm long stainless steel tubes with 1/8 in. outer diameter and 1.75 mm inner diameter,

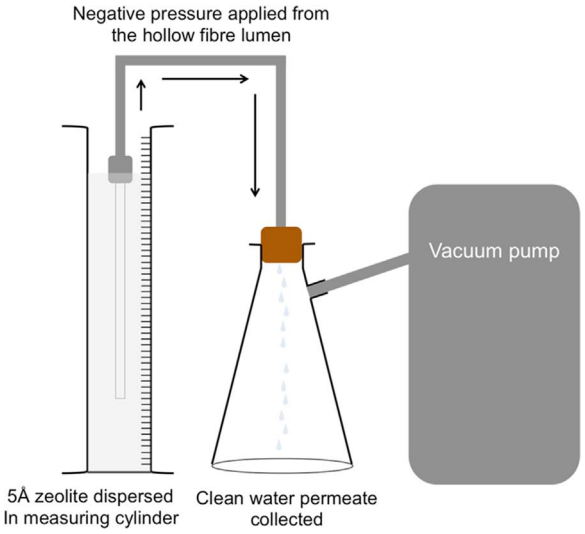

Fig. 2. The set-up for depositing zeolite into the hollow fibre micro-channels via vacuum suction.