Chemical Engineering Science 94 (2013) 256–264

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

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

Dual layer hollow fiber sorbents for trace H_2S removal from gas streams

Dhaval A. Bhandari [1], Naoki Bessho, William J. Koros *

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 778 Atlantic Drive, Atlanta, GA 30332-0100, United States

HIGHLIGHTS

- Hollow fiber sorbents show high H_2S sorption capacity.
- Fibers indicate macroscopic pores due to both polymer and suspended zeolites.
- Higher zeolite loading fibers spun at lower dope temperature show higher porosity.
- Polyvinylidene chloride (PVDC) barrier sheath layer found to give low gas permeance.

ARTICLE INFO

Article history:
Received 18 November 2012
Received in revised form
2 February 2013
Accepted 1 March 2013
Available online 13 March 2013

Keywords:
Adsorption
Membranes
Separations
Polymer processing
Dual-layer hollow fibers
Mercury porosimetry

ABSTRACT

Hollow fiber sorbents are pseudo monolithic materials with potential use in various adsorption based applications. Dual layer hollow fiber sorbents have the potential to allow thermal regeneration without direct contact of the regeneration fluid with the sorbent particles. This paper considers the application of dual layer hollow fiber sorbents for a case involving trace amounts of H_2S removal from a simulated gas stream and offers a comparison with single layer hollow fiber sorbents. The effect of spin dope composition and core layer zeolite loading on the gas flux, H_2S transient sorption capacity and pore structure are also studied. This work can be used as a guide to develop and optimize dual layer hollow fiber sorbent properties beyond the specific example considered here.

1. Introduction

The motivation of the work is to enable use of natural gas for on-site reforming to produce hydrogen for filling stations. Since pipeline natural gas contains trace levels of residual H_2S and other organic sulfur species up to 30 ppm intentionally added as odorants to detect leaks; these sulfur compounds need to be removed effectively to prevent poisoning of metal catalysts in the reforming process. For low concentration and small scale systems, highly energy intensive processes like amine absorption and hydrodesulfurization (HDS) are less attractive. Traditionally, packed bed adsorbents such as zeolites, activated carbon and metal oxides have been applied for this application (Kang et al., 2007; Kim et al., 2007; Weber et al., 2008).

Structured monoliths with high sorbent loadings have the potential to economically replace conventional pellet packed bed technology. The advantages of these structures include lower pressure drop, higher surface area to volume ratio and improved mass transfer characteristics (Bhandari et al., 2010; Lively et al., 2009). Pseudo-monolithic separations materials called fiber sorbents can be created with fiber spinning technology using a polymer ‘binder’, impregnated with high loadings of zeolite sorbent ‘fillers’ (Bhandari et al., 2010). Single layer hollow fiber sorbents for low concentration sulfur removal have been developed using cellulose acetate (CA) binder polymer and zeolite NaY as sorbent particles, and their regenerability has been demonstrated by temperature swing adsorption (TSA) (Bhandari and Koros, 2009; Lively et al., 2012). Steam or hot gases were found to be the preferred heat transfer media for heating; however, the capacity of hydrophilic zeolite decreases considerably when in direct contact with water vapor or steam.

It is desired to obtain a defect-free, dense sheath layer with low permeability, while simultaneously obtaining a highly porous core layer to provide a sulfur sorption capacity that is determined

* Corresponding authors. Tel.: +1 404 385 2845; fax: +1 404 385 2683.
E-mail address: wjk@chbe.gatech.edu (W.J. Koros).
[1] Currently at GE Global Research, Niskayuna, NY.

0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2013.03.003

by the dry zeolite loading. To enable creating a workable material, a low permeability, thin polymer barrier layer on the outside of fiber sorbents (sheath) is needed to only allow thermal interactions of the sorbent particles with the regeneration media, thereby promoting consistent sorption capacity over repeated cycles. In the proposed module operation, pipeline natural gas with sulfur impurities will be fed to the bore (or lumen) side while the regeneration fluid (steam or hot gas) will be fed on the shell side. The low permeability sheath layer will allow only thermal interaction with the regeneration fluid while limiting mass transfer which could reduce the sorbent capacity. A bore feed provides an advantage of lower bypass and channeling (compared to a shell feed), which is crucial for the effective operation of this technology. Typically, metal catalysts used in fuel processing and in fuel cell electrodes are irreversibly poisoned by sulfur compounds above a concentration of 1 ppm (Kang et al., 2007).

Previous work has shown that delamination free dual layer fiber sorbents with a low permeability polyvinylidene chloride (PVDC) sheath layer can be successfully synthesized by simultaneous co-extrusion through a triple orifice spinneret die (Bhandari et al., 2012). Fig. 1 shows the schematic representation of single and dual layer fiber sorbents while Fig. 2 shows the actual fabricated CA/NaY single layer and CA/NaY-PVDC dual layer fiber sorbents.

The goal of this paper is to characterize the various fabricated fiber sorbent materials for their ability to remove trace amounts of sulfur impurities from a simulated gas stream. Mercury porosimetry was used to characterize the average pore size and fiber porosity and transient H_2S sorption studies were used to determine its sorption performance. Gas permeability studies allowed analysis of the gas flux through the fiber under a pressure gradient as an indirect measure of transport resistances in the porous single layer fiber to complement conventional porosimetry and in dual layer fibers to check barrier sheath layer efficacy. The three characterization techniques give a valuable picture of dual layer fiber sorbent properties, provide performance comparison with single layer fiber sorbents and clarify the effect of the low permeability sheath layer on the resultant zeolite sorbent loaded core layer morphology.

2. Materials and experimental methods

2.1. Materials

The materials screened and selected for the development of dual layer hollow fiber sorbents were described previously (Bhandari et al., 2012), however the key materials are summarized here for the sake of clarity and completeness. Cellulose acetate (CA) ($M_n \approx$ 50,000, Sigma-Aldrich, Milwaukee, WI), was selected as the core layer binder polymer, while zeolite NaY (CBV-100, Si/Al = 2.6, average crystal size = 300–700 nm, Zeolyst, Valley Forge, PA) was selected as an H_2S selective sorbent. CA has a relatively high glass transition temperature (T_g), is inexpensive and has tailorable properties based on the degree of acetylation and molecular weight (Puleo et al., 1989), while zeolite NaY is commercially available in small particle sizes with high sorption capacity for sulfur gases.

Polyvinylidene chloride (PVDC) (IXAN® PNE-288, VDC/MA copolymer, $M_n \approx 40{,}600$, PDI = 2.6, Solvay Advanced Polymers, Alpharetta, GA) was screened as the material of choice for the sheath layer. Polyvinylpyrrolidone (PVP) was added to the core and sheath dopes. A low molecular weight PVP leaches out rapidly forming a porous structure as desired in the core layer morphology. On the contrary, high molecular weight PVP has been found to leach out slowly during solvent exchange and in certain cases block some of the interconnected pores as desired in a dense sheath layer (Duarte, 2002; Qin et al., 2003). Hydrophilic PVP can also enable better compatibility between the core and sheath dopes and also enhance the viscosity reducing macro void formation. CA/NaY single layer and CA/NaY-PVDC dual layer fiber sorbents were spun successfully with up to 75 wt% and 65 wt% core layer zeolite loadings (dry fiber wt% basis) respectively. The core and sheath spin dope compositions used to synthesize single and dual layer fiber sorbents are summarized in Tables 1 and 2.

2.2. Sorption measurement system and testing procedure

Testing of fiber sorbents under realistic flow conditions is important to determine applicability as a new separations platform. A single/dual layer fiber sorbent with minimal mass transfer resistance should give sorption capacity (normalized based on its sorbent loading) similar to pure zeolite particles. A lab testing rig was designed and constructed to conduct the sorption tests (Fig. 3).

The test rig and lecture bottles of a model sulfur containing gas comprising 30 ppm H_2S/N_2 mixture were located inside a fume hood for safety reasons. Teflon® tubing (1/8 in. O.D., 1/16 in. I.D., McMasterCarr, Atlanta, GA) was used to prevent significant sorption on the working surfaces of the system. Sulfur alarms were installed in the fume hood and near the sulfur analyzer to detect any sulfur leakage. H_2S/N_2 gas passed through a flow controller (Model: FMA-A2305-SS, Omega engineering Inc., Stamford, CT) to obtain a desired flow rate between 0–500 sccm. The sulfur gas concentration could be further diluted by the addition

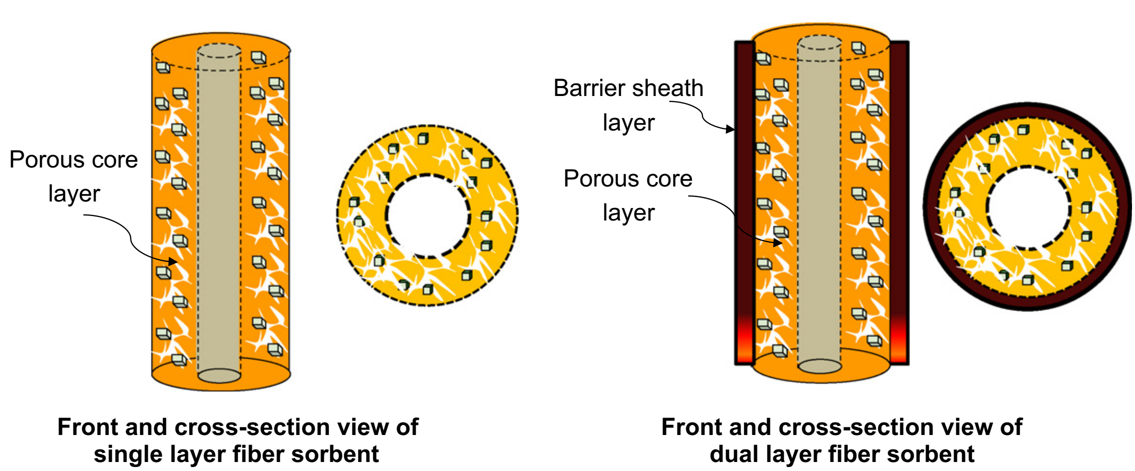

Fig. 1. Schematic diagram showing the key features of a single and dual layer hollow fiber sorbent.