Heterogeneous membranes filled with hypercrosslinked microparticle adsorbent

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Abstract

Synthesis of hypercrosslinked microparticles is described and the effect of reaction conditions on adsorbent properties is discussed. Heterogeneous membranes based on hypercrosslinked microparticle adsorbent with a poly(phenylene oxide) binder were prepared and tested for separation of hydrogen from a isobutane/hydrogen mixture. The separation process was characterized by parameters, such as diffusion flux, permeability, and selectivity. The prepared membranes were superior to the homogeneous ones in permeability and to zeolite-filled membranes in selectivity. Selectivity reached values of about 540 in H_2/isobutane separation.
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1. Introduction

Membrane separations are frequently used in separation technologies in a permanent competition with alternative methods such as adsorption and column technologies. Membrane separations pre-vail in large-scale processes enabling automation. The development of heterogeneous membrane dates back long before homogeneous membranes, but not much publicity was given to heterogeneous membranes based on polymeric adsorbents.

1.1. Membrane components

In order to enhance permeability and selectivity of polymer membranes, many different adsorbents

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have been incorporated in the polymer matrix [1,2]. Adsorbents include zeolites, molecular sieves, activated carbon and even colloidal particles.

Pervaporation membranes for removal of volatile organic compounds from waste water were prepared by Sikdart et al. [3]. The polymeric membrane used was filled with a hydrophobic adsorbent of a high surface area. The adsorbent was used in the amount 1–25 wt% of the total membrane weight. The polymeric membrane was made of polymers, such as poly(dimethylsiloxane), poly[1-(trimethylsilyl)prop-1-ene)], polyurethane, polybutadiene, poly(ether-*block*-amide), silicone-polycarbonate, poly(styrene-*co*-butadiene), poly(acrylonitrile-*co*-butadiene), and poly(ethylene-*co*-propylene). Activated carbonaceous adsorbents, zeolites, and molecular sieves made by polymer pyrolysis, and polymer resins were used as adsorbents.

1.2. Separations

Heterogeneous membranes with 1–25 wt% of an adsorbent were used as pervaporation membranes for removal of volatile organic compounds from water [4,5]. Permselective membrane modules [6] were tested for separation of organic solvent vapours from waste gases. As adsorbents zeolites, activated carbon, organic polymer fibres or activated carbon fibres were used. Also gas-phase separations [7,8] were studied by using heterogeneous composite membranes. Poly(dimethylsiloxane) (PDMS) membrane filled with carbonaceous molecular sieve (CMS) or silicalite [9,10] exhibit low selectivity improvements compared with the rubbery polymer matrix (about 20–55 wt%). The chosen CMS adsorbents show selectivity for a oxygen–nitrogen mixture, which complements the equilibrium oxygen–nitrogen selectivity of silicone rubber. The best results were obtained with the PDMS-CMS membrane containing about 50% CMS by volume. Possible reasons for a low-selectivity increase include low O_2/N_2 selectivity of the starting CMS (Cecalite, W20, and Carbosieve) and loss in selectivity during size reduction. Further improvements in selectivity are possible using a polymer matrix with higher selectivity and by increasing adsorbent loading.

Lee et al. [11] presented a fundamental study on the prediction of breakthroughs in a continuous flow membrane system containing powdered activated carbon (PAC) for phenol removal. Typically, adsorption isotherm of phenol on PAC typically was described by the Freundlich equation. A model of surface diffusion was successfully used to simulate the adsorption of phenol in the systems. Intraparticle transport appeared to be the rate-limiting step. The surface diffusivity obtained by fitting the model breakthrough curve to experimental data was 3.3×10^{-8} cm^2/s.

Attention has also been paid to the theory of mass transport in heterogeneous membranes containing adsorbent particles suspended in the continuous matrix of a polymer [12]. Monotonically increasing or decreasing permeabilities of composite membrane are well described by these models.

Homogeneous membranes (polysulfones, ethylcellulose, polyimides, etc.) with moderately good selectivity for separation of air components tend to have low permeability requiring either a large membrane area or very thin separation layer or both.

1.3. Hypercrosslinked resins

Crosslinking linear polymers or swollen gel-type or macroporous copolymers affords hypercrosslinked resins using Friedel–Crafts alkylation or acylation. Typical crosslinking agents for polystyrene or low-crosslinked styrene-divinylbenzene copolymers include chloromethyl methyl (or ethyl) ether [13,14], chloromethyl polyethers [15], *p*-xylylene dichloride [16,17] α,α-dichloro-*p*-xylene [18], 4,4′-bis(chloromethyl)biphenyl [19], dimethylformal [19], tris-(chloromethyl)mesitylene [19], 1,4-bis(4-chloromethylphenyl)butane [19], sulfur halides [20], 1,4-bis(chloromethyl)-2,5-dimethylbenzene, 2,4,6-tris-chloromethyl-mesitylene, adipoyl dichloride, 1,4-bis(acetoxymethyl)-2,5-dimethylbenzene, 1,4-bis(hydroxymethyl)benzene, and tetrachloromethane [20]. As catalysts, tin (IV), iron (III) and titanium (IV) chlorides are used.

In the three-dimensional networks, the linear polymer chains are interconnected by a separate