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Rapid communication

Hydrocarbon/hydrogen mixed-gas permeation properties of PIM-1, an amorphous microporous spirobisindane polymer

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ABSTRACT

The gas permeation properties of the microporous glassy ladder polymer PIM-1 are reported for hydrocarbon/hydrogen mixtures. PIM-1 is more permeable to hydrocarbon vapors than to hydrogen, a behavior similar to that of the microporous linear-chain poly(1-trimethylsilyl-1-propyne) [PTMSP]. For a 2 vol.% *n*-butane/98 vol.% hydrogen feed mixture, PIM-1 has a mixed-gas *n*-butane permeability of 4000 Barrer combined with an *n*-butane/hydrogen selectivity of 27. An increase in *n*-butane feed concentration leads to an increase in *n*-butane permeability, but has only a minor effect on the hydrogen permeability. As a result, the *n*-butane/hydrogen selectivity increases from 27 to 51 as the feed *n*-butane concentration increases from 2 to 7.3 vol.%. Because of its excellent mixed-gas hydrocarbon/hydrogen selectivity and high permeability, PIM-1 could find use as a novel membrane material in petrochemical applications, such as hydrogen recovery from fluid catalytic cracker off-gases.

1. Introduction

Membrane-based gas separation is a well-established unit operation in the petrochemical industry. Specifically, the recovery of hydrogen from a variety of feed streams containing permanent gases, such as methane and carbon monoxide, has been successfully applied using size-selective, glassy polymer membranes that are more permeable to hydrogen than to the other feed gas components [1–5]. However, this type of separation usually requires recompression of the hydrogen-enriched permeate, which renders the process uneconomic in many cases [6]. The recovery of hydrogen from large, condensable C_{3+} hydrocarbons is also a separation of considerable interest. For example, fluid catalytic crackers produce off-gas streams that contain 10–30 vol.% hydrogen in mixtures with higher hydrocarbons. Currently, these valuable hydrogen-containing off-gas streams are mainly used as fuel. Conventional rubbery membranes, such as poly(dimethylsiloxane) [PDMS], are hydrocarbon-vapor-selective, enabling hydrogen to be captured in the high-pressure residue product stream [6,7]. However, PDMS membranes have only moderate selectivity for hydrocarbons over hydrogen, making their use only marginally economical. Higher C_{3+} hydrocarbon/hydrogen selectivities are required for membrane processes to be competitive with conventional separation technologies, such as cryogenic condensation or pressure swing adsorption.

About 10 years ago, it was reported that microporous glassy acetylene-based polymers, such as poly(1-trimethylsilyl-1-propyne) [PTMSP], exhibit excellent properties for organic vapor/gas separations, including hydrocarbon/hydrogen separation [8–10]. For a feed mixture containing 2 vol.% *n*-butane in hydrogen, PTMSP has an *n*-butane permeability of about 40,000 Barrer coupled with an *n*-butane/hydrogen selectivity of 24 [9]. Because of its outstanding separation properties, PTMSP was initially considered to be a promising membrane material for C_{3+} hydrocarbon/hydrogen applications. Unfortunately, it was found to have very poor chemical resistance to hydrocarbon liquids, and cannot be used in these industrial applications.

Recently, Budd et al. and McKeown et al. developed a new class of high-free-volume glassy ladder polymers and named them “polymers of intrinsic microporosity” (PIMs) [11–15]. These spirobisindane-based polymers have a highly contorted structure that hinders any rotations in the polymer backbone. As a result, PIMs have large BET surface area and very high gas permeability [11–15]. To date, the most detailed permeation studies have been performed on PIM-1, which is a polycondensation product of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and tetrafluoroterephthalonitrile; the structural repeat unit of the polymer is shown in Fig. 1.

In a previous paper, we reported that PIM-1 exhibits very good properties for the separation of *n*-butane/methane mixtures, an

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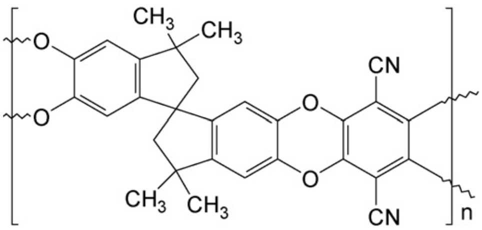

Fig. 1. Repeat unit of PIM-1.

important application for heating value and dew point control of natural gas [16]. In the present work, the possible use of PIM-1 as a membrane material for recovery of hydrogen and/or hydrocarbons in petrochemical applications is discussed. The gas permeation properties of PIM-1 are reported for hydrocarbon/hydrogen mixtures and compared to those of a microporous acetylene-based polymer (PTMSP).

2. Experimental

2.1. Polymer film preparation

PIM-1 was synthesized as described in a previous paper [17]. Isotropic, dense films were prepared by slowly pouring a filtered 2 wt.% chloroform solution of the polymer in a flat-bottomed glass Petri dish. The dish was covered with a glass plate to slow the rate of solvent evaporation. The films were dried at ambient temperature until evaporation of the solvent was complete and then removed from the Petri dish and placed in a vacuum oven at 70 °C to remove any residual solvent. Thereafter, the films were immersed in methanol for 2 h at ambient conditions to reverse any prior film formation history. After removal from methanol, the films were dried gradually at 70 °C in air. Methanol preconditioning ensures the preparation of PIM-1 samples with reasonably reproducible gas permeation properties [15,16]. The film used for the permeation experiments had a thickness of 55 μm. Other physical properties, such as density and fractional free volume, have been reported in an earlier publication [16].

2.2. Gas mixture permeation measurements

Mixed-gas permeation measurements were carried out at 25 °C with *n*-butane/hydrogen mixtures using the constant pressure/variable volume method [7]. The *n*-butane concentration in the feed mixture was varied between 2 and 7.3 vol.%. All experiments were performed at a feed pressure of 150 psig; the permeate pressure was atmospheric (0 psig). The residue and permeate compositions were determined using a gas chromatograph equipped with a TCD detector. The stage cut (the ratio of permeate to feed flow rate), was always kept below 1%. Under these conditions, the residue composition is essentially equal to the feed composition. Mixed-gas permeances and selectivities were calculated as described in previous papers [7,16].

Table 1
Mixed-gas permeation properties for PIM-1 and PTMSP. Feed: 2 vol.% *n*-butane in hydrogen; feed pressure: 150 psig; permeate pressure: 0 psig; temperature: 25 °C.

Material	Permeability (Barrer)		Selectivity $n\text{-}C_4H_{10}/H_2$	H_2 mixed-gas/pure-gas permeability ratio
	$n\text{-}C_4H_{10}$	H_2		
PIM-1	4000	150	27	0.04
PTMSP[a] [9]	40,000	1650	24	0.10

[a] Feed pressure for PTMSP: 200 psig.

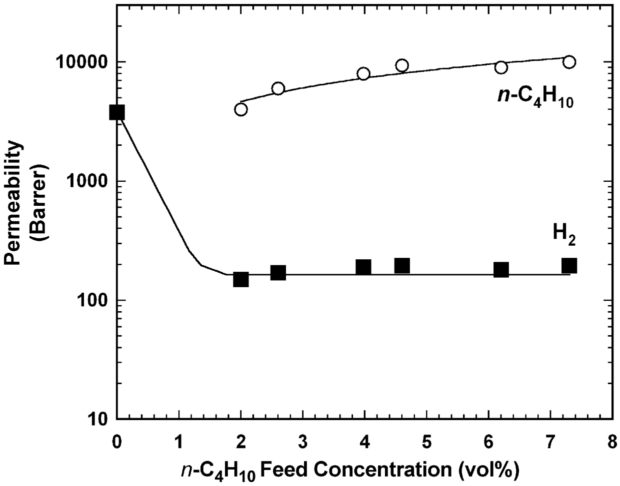

Fig. 2. Mixed-gas hydrogen and *n*-butane permeability of PIM-1 as function of *n*-butane feed concentration. Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); temperature: 25 °C.

3. Results and discussion

3.1. Separation of binary *n*-butane/hydrogen mixtures

PTMSP, the first reported polymer of intrinsic microporosity, is “reverse-selective”, that is, it is more permeable to large, condensable hydrocarbons than to small permanent gases, such as methane, nitrogen or hydrogen. For C_{3+} hydrocarbon/methane and C_{3+} hydrocarbon/hydrogen separations, PTMSP shows the highest hydrocarbon permeabilities combined with the highest selectivities of all known polymers [8–10].

The gas permeation properties of PIM-1 for a feed mixture containing 2 vol.% *n*-butane in hydrogen are compared to those of PTMSP in Table 1. At 150 psig and 25 °C, the *n*-butane/hydrogen selectivities of PTMSP and PIM-1 are 24 and 27, respectively. Interestingly, PIM-1 shows 10-fold lower mixed-gas *n*-butane permeability than PTMSP. This result is surprising as both polymers have essentially the same free volume based on BET surface area measurements [18,19]. However, Staiger et al. recently reported that PIM-1 has a significantly smaller fraction of large free volume elements than PTMSP based on positron annihilation lifetime spectroscopy data [20], which could explain its lower gas permeability.

Microporous materials such as PTMSP or carbon are characterized in mixed-gas experiments by blocking (reduction in mixture permeability relative to pure-gas permeability) of the small permanent gases by larger condensable feed components [9]. The same blocking effect was observed in PIM-1 for *n*-butane/hydrogen mixtures. The permeability of hydrogen through PIM-1 is greatly reduced by co-permeation of *n*-butane; the hydrogen mixed-gas permeability is only about 150 Barrer, which is 25-fold lower than the pure-gas hydrogen permeability of 4000 Barrer.

The mixed-gas permeation properties of PIM-1 were studied as a function of the *n*-butane concentration in the feed mixture. Mixtures of 2–7.3 vol.% *n*-butane in hydrogen were used to perform the experiments. The *n*-butane and hydrogen permeabilities and the *n*-butane/hydrogen selectivity of PIM-1 as a function of the feed composition are shown in Figs. 2 and 3, respectively. As the *n*-butane feed concentration increases from 2 to 7.3 vol.%, the *n*-butane permeability increases 2.5-fold from 4000 to 10,000 Barrer, whereas the hydrogen permeability is essentially constant around 150–200 Barrer. The increase in *n*-butane/hydrogen selectivity is due to swelling-induced dilation of the polymer matrix, which leads to a decrease in the hydrogen/*n*-butane diffusivity selectivity. Swelling affects both *n*-butane and hydrogen diffusion,