Chemical Stability of Polyimide Membranes at Temperatures Near T_g

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SYNOPSIS

The success of polymeric membranes for use in high temperature gas separation applications relies, in part, on the chemical stability of these materials in separation environment. This paper details experimental evaluation of the stability of membranes prepared using a polyimide as the selective separating layer when exposed to butane/butene/hydrogen mixtures at temperatures near the glass transition temperature of the polymer, 310°C. Further, the effects of small concentrations of sulfur and ammonia compounds in the feed mixture were investigated, as was the influence of a simulated air leak. The gas transport rates and selectivities were unchanged when testing in the hydrocarbon/hydrogen environment for over 30 days. Further, no changes in transport properties were observed when hydrogen sulfide or ammonia was added to the feed mixture. However, degradation due to oxygen exposure was observed. The chemical stability of the polyimide layer appears to be sufficient to be utilized for the separation of high temperature petrochemical streams. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The development of membranes for high temperature gas separation has produced a class of hybrid composite materials with both organic and inorganic components.[1-6] The configuration of these materials varies greatly, ranging from a dense metal layer supported on silicone rubber[1] to thin polymeric layers supported on highly porous ceramic supports.[2-4,6] To date, these materials have remained in the development stages. However, the outstanding separating properties previously reported for polyimide–ceramic composite membranes for the removal of hydrogen from hydrocarbon systems at 300°C have provided strong motivation to evaluate the ability to move the development of these materials forward. We have previously demonstrated the utility of these membranes to dramatically improve the operation of butane dehydrogenation reactors.[7]

The success of polymeric membranes for use in reactor applications and other high temperature gas separation applications relies, in part, on the stability of these materials in the separation environment. The chemical stability and tendency of the organic polymer layer to absorb materials from the process stream can have adverse effects on separation performance of polymeric layers in composite membranes. These absorbed materials may then be involved in chemical reactions with the polymeric material. The detailed effects of these changes are difficult to predict, a priori. Therefore, experimental evaluation of the stability of the polymer layer in the presence of materials that are commonly present in a typical hydrocarbon stream of a membrane-assisted dehydrogenation reactor has been completed. This study was carried out as part of a larger program to evaluate the utility of these membranes for the separation of hydrogen from a butane dehydrogenation reaction product mixture.[8] The components and concentration of this system governed the choice of feed compositions evaluated.

Stability was measured by exposing membranes to a variety of chemical environments at 300°C, just below the polymer's glass transition temperature.
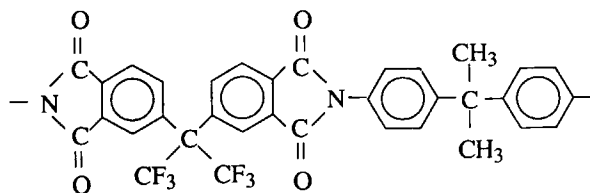

Figure 1   Structure of the 6FDA-IPDA repeat unit.

The gas transport properties were monitored as a function of exposure time. Results are presented in terms of the hydrogen permeability, and hydrogen/ hydrocarbon selectivity of the membrane as a function of exposure time to the feed stream in question. Changes in the physical structure of a very small fraction of the polymeric material can lead to significant changes in the gas transport properties of the membranes.[9] Therefore, this technique was chosen as a simple, sensitive measure of a relatively large surface area of sample.

BACKGROUND

The rate of gas transport through membranes is shown mathematically in eq. (1).

$$Q = \frac{P \Delta p A}{l} \qquad (1)$$

where Q is the permeation rate (cm^3/s), P is the permeability coefficient of the membrane material for the given penetrant [$cm^3(STP)$ $cm/(s$ cm^2 $cmHg)$], A is the area of the membrane (cm^2), l is the effective membrane layer thickness (cm), and Δp is the partial pressure driving force across the membrane (cmHg).

The thickness and perfection of the membranes can be measured by monitoring the relative transport rates of two gases through the membrane. If transport is restricted to the solution-diffusion mode, indicating a lack of pores or defects in the sample, the relative ratio of these two rates, denoted α as in eq. (2), will be identical to that measured on a macroscopically thick sample of the material if identical process conditions are employed.

$$\alpha_{A/B} = \frac{Q_A}{Q_B} \qquad (2)$$

If defects are present in the surface of the sample, gas can be transported through the membrane by either a Knudsen or bulk flow mechanism. The selec-

tivity, α, of these modes of transport is significantly lower than the selectivity achieved by nonporous films of the polymer. Therefore, any value less than that achieved by the thick film is an indication of the presence of pores, or defects, in the membrane. The use of gas transport measurements has been shown to be extremely sensitive to the presence of defects at concentrations of less than 1 ppm.[9]

EXPERIMENTAL

Materials

Polymer–Ceramic Composite Membrane

Polymer–ceramic composite membranes were employed because they offer the special possibility to monitor chemical changes in the thin polymer layer directly. These membranes were prepared by a solution deposition method using the thermally stable 5,5'-[2,2,2,-trifluoro-1-(trifluormethyl)ethylidene]bis-1,2-isobenzofuran-dione, isopropylidenedianiline (hereafter called, 6FDA-IPDA) polyimide as the polymer layer and porous ceramic filters as the substrates.[6] The structure and room temperature properties of this polymer are shown in Figure 1 and Table I. Porous ceramic filters with a surface pore size of approximately 200 Å, commercially marketed by Anotech Separations under the trade name Anopore® were used as the substrate layer. Each membrane was evaluated at room temperature for the separation of helium from nitrogen, using a constant pressure–variable volume test system[10] to determine both the perfection and thickness of the polymer layer. Only membranes with helium/nitrogen selectivities equivalent to that of a dense films of the polymer were used for further evaluation, unless otherwise indicated. Effective polymer layer thicknesses were on the order of 0.1–1.0 μm.

Gases

Instrument-grade normal butane (minimum purity of 99.5 mol %), ultrahigh purity grade hydrogen

Table I   Physical Properties of 6FDA-IPDA Polyimide at 25°C

Glass transition temperature, T_g	310°C
Density, ρ	1.352 g/cm^3
Permeability to helium, P_{He}	62.5 Barrer
Permeability to nitrogen, P_{N_2}	1.33 Barrer
Selectivity for He/N$_2$ separation, α_{He/N_2}	47.0

1 Barrer = [1 × 10^{-10} cm^3(STP) cm]/s cm^2 cmHg.

Table II Compositions of Gas Mixtures (mol %) Used to Test the Chemical Stability of the Membranes

Mixture	n-Butane	Hydrogen	Hydrogen Sulfide	Ammonia
Base case	75.0	25.0	—	—
H_2S	75.0	24.75	0.25	—
NH_3	75.0	24.9737	—	0.0263

(minimum purity of 99.99 mol %), and certified mixtures of hydrogen with 1.0 mol % hydrogen sulfide and hydrogen with 0.105 mol % ammonia were purchased from Matheson Gas products and used as received without further purification.

Equipment

Mixed gas permeation measurements were completed in the constant volume–variable pressure permeation cell employed in our labs[11] with a permeate pressure of less than 20 Torr and a total feed pressure of 15.8 ± 0.1 psia. For measurement at temperatures up to 300°C, a commercially supplied test cell (Millipore Corporation, Bedford, MA) was employed. The cell was sealed with either Kal-rez® or Teflon® gaskets, which were temperature stable to approximately 320°C. A membrane area of 13.8 cm² was used for all testing. The feed flow was maintained at or above 21 cm³ (STP)/min.

The concentrations of the feed, permeate, and retentate were measured using a Tracor 570 gas

Figure 2 Stability of polyimide–ceramic composite at 270°C in the presence of butane–hydrogen mixtures and butane–hydrogen–hydrogen sulfide mixtures. Closed diamonds, data points. Open diamonds, error at each point.

chromatograph equipped with a thermal conductivity detector (TCD). The gases were separated in a $\frac{1}{8}$-in. stainless steel column 5 feet in length and fed to the TCD via a helium carrier gas. The column, packed with Carbosieve S-II, 100/120 mesh, was incapable of resolving the hydrocarbon mixture, therefore all analysis is presented in terms of hydrogen and total hydrocarbon concentration.

Procedure

Polyimide–ceramic composite membranes were placed in a gas permeation test cell with a Kal-rez® o-ring placed on their surface at 25°C. Nitrogen was fed to the membrane surface and a vacuum was pulled on the permeate side. This open system was heated to the test temperature and, at that temperature, the cell was closed establishing a seal between the feed and permeate sides of the membrane. The membrane was maintained under nitrogen flow until testing was initiated. The gas transport properties of the membrane in the presence of the gas mixtures shown in Table II were measured for a period of at least 70 h.
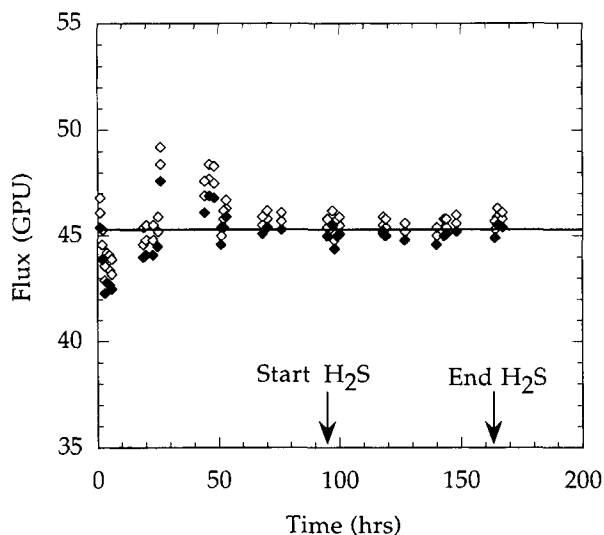
RESULTS AND DISCUSSION

Exposure to Hydrogen/Butane Mixture

The gas transport rates and selectivity for the separation of hydrogen from butane appear to be unaffected by continued exposure to this gas mixture at high temperatures. Gas permeation measurements were completed for approximately 100 h under continuous feed of a mixture of 25 mol % hydrogen and 75 mol % normal butane. During this time period, the mixed-gas flux and selectivity were essentially constant. These results are presented in Figure 2 and detailed in Table III.

Two, more extensive, evaluations were made during actual integrated membrane-reactor operation.[7] The membranes were heated to between 250 and 300°C under a nitrogen environment and then switched to separate the reactor effluent. Direct

Table III   Effect of Hydrogen Sulfide Exposure on the Hydrogen/Butane Selectivity of a Polyimide–Ceramic Composite Membrane at 270°C

Feed Conditions	Total Time on Line (hr)	Mixed-Gas Selectivity[a]
Hydrogen/butane	90	95
Hydrogen/butane/H$_2$S	110	103
Hydrogen/butane/H$_2$S	135	96
Hydrogen/butane/H$_2$S	150	> 120
Hydrogen/butane	170	105

[a] Selectivity = (hydrogen$_{permeate}$/butane$_{permeate}$)/(hydrogen$_{feed}$/butane$_{feed}$) Stage cut ≈ 0.90.

comparison of the stability of the membrane fluxes is not possible in these tests, as the composition of the feed stream changed as a function of time and catalyst activity. However, the ability of these membranes to selectively remove hydrogen while removing a minimum amount of hydrocarbons has been demonstrated by the improvement in reactor performance.[7] The first membrane operated successfully at 300°C for 32 days, the second at 250°C for 16 days. Membrane performance following these test periods was still satisfactory. The membranes were removed to allow for testing of other materials, not because of degradation of performance. These results indicate that the membranes were not adversely affected by extended exposure to high temperature hydrocarbon mixtures.

Exposure to Air

Membrane

Following the above evaluation, the feed to the second membrane was switched from hydrocarbon to nitrogen. The temperature was held at 250°C for 40 days with approximately 2 psig nitrogen on the feed side and atmospheric air on the permeate. The membrane was removed from the test cell and evaluated at room temperature. The properties before and after this extended heating period are shown in Table IV.

The gas transport rate of this membrane was essentially constant during the period of exposure to the hydrogen/hydrocarbon mixture. However, following the high temperature exposure with atmospheric air on the permeate side, the membrane lost selectivity and the gas transport rates increased significantly. During this time period, nitrogen was fed to the membrane at pressures slightly above atmo-

spheric and allowed to permeate to a receiver held at atmospheric pressure. While the permeation rate under these conditions is quite high (above 73 GPU; 1 GPU = 10^{-6} cm^3 (STP)/cm^2 sec cmHg), diffusion of air into the permeate volume and ultimately into the membrane was possible. This oxygen could have reacted with the polymer during this extended period at high temperature and created the changes observed in the gas transport properties. Similar oxygen degradation reactions have been observed in chemically similar polyheteroarylenes at slightly higher temperatures, but over a much shorter time period.[12]

Polymer

The response of powder samples of the 6FDA-IPDA polyimide to heating were analyzed using a Seiko Thermal Gravametric Analyzer. In the analysis, samples of the polymer were heated in a stream of flowing nitrogen or air. The weight of the sample was recorded as a function of temperature of the sample. The relative weight at each temperature is reported. In this analysis, the temperature of the chamber was increased from 40 to 500°C at a rate of 20°C/min. The flow rates of nitrogen and air were maintained at 300 ± 50 cm^3(STP)/min.

The relative weight of the 6FDA-IPDA sample heated in nitrogen is nearly constant over the entire temperature range. In contrast, exposure to air at temperatures above 400°C caused a marked weight loss in the polyimide sample, as shown in Figure 3. This observation provides further understanding to the loss in permselectivity of samples heated in the presence of air.

Exposure to H$_2$S

Membranes exposed to mixtures of hydrogen and butane with approximately 2500 ppm hydrogen sul-

Table IV   Effect of Heating Polyimide–Ceramic Composite Membrane to 250°C under Hydrogen/Butane and Nitrogen/Air Mixtures for a Total of 60 Days[a]

Prior to High Temperature Exposure		After High Temperature Exposure to Air	
Nitrogen Flux (GPU)	α He/N$_2$	Nitrogen Flux (GPU)	α He/N$_2$
4.7	44.0	27.2	13.2

[a] Sixteen days under hydrocarbon feed, vacuum permeate, 44 days under nitrogen feed, atmospheric permeate.
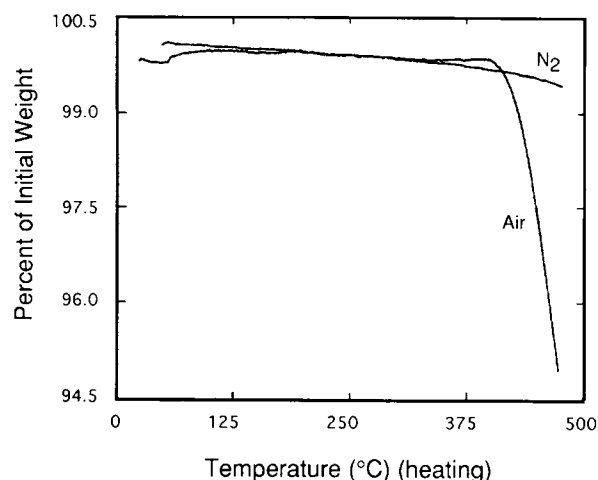[b] GUP = [10^{-6} cm^3 (STP)]/(cm^2 s cmHg).

Figure 3 Weight loss of 6FDA-IPDA polyimide as a function of exposure temperature and environment.

fide exhibited gas transport rates and hydrogen/butane selectivities equivalent to those of the nonsulfated feed. Exposure of a selective membrane to this gas mixture at 270°C resulted in no change in the overall membrane properties. The total membrane flux for this mixed gas stream is shown in Figure 2. Although there is some scatter in the data in the early phases of the nonsulfated feed tests, the overall flux prior to introduction of hydrogen sulfide, during exposure, and following the removal of hydrogen sulfide from the feed is essentially constant at about 45.5 GPU.

The selectivity of the membrane for the separation of hydrogen from hydrocarbon during each of these phases is presented in Table III. Again constant properties are observed. No measure of the hydrogen/hydrogen sulfide selectivity was made for this analysis.

These results indicate that at least for the exposure period tested, the hydrogen sulfide is not interacting with the polymer layer and producing a change in its chemical or physical structure. This test was completed for a total exposure time to hydrogen sulfide of approximately 70 h. In practice, if these membranes were to find use in a membrane-assisted reactor system, the effects of the sulfur compounds on reactor performance would be quite devastating.[13] Therefore, changes in the overall system operation would be readily observed in evaluation of product quality. Measures to reduce any high exposure levels of hydrogen sulfide would almost certainly be taken within an hour of the initial exposure. Since the membrane is much less sensitive to the exposure of hydrogen sulfide, and is apparently unaffected by the compound for times up to

70 h, it is expected to perform well in these environments.

Exposure to NH₃

Membranes exposed to mixtures of hydrogen and butane with approximately 263 ppm ammonia exhibited gas transport rates and hydrogen/butane selectivities equivalent to those of the ammonia-free feed. Exposure of a selective membrane to this gas mixture at 250°C resulted in no change in the overall gas transport rates or selectivity, as is detailed in Figure 4 and Table V.

The stability of the membrane in the presence of ammonia indicates that at least for the time period studied, no destructive reactions between the polymer and the ammonia were observed. Ammonia and sulfur are temporary catalyst poisons and following their removal from the feed, the activity of the catalyst commonly returns to the preexposure levels.[13] Rapid catalyst deactivation in the presence of ammonia is expected and the membrane stabilities measured should be sufficient for use in the proposed membrane-assisted dehydrogenation systems.

CONCLUSIONS

This evaluation has provided analysis of the chemical stability of a 6FDA-IPDA polyimide in various gaseous components at temperatures near the polymer T_g. No changes in the polymer properties were
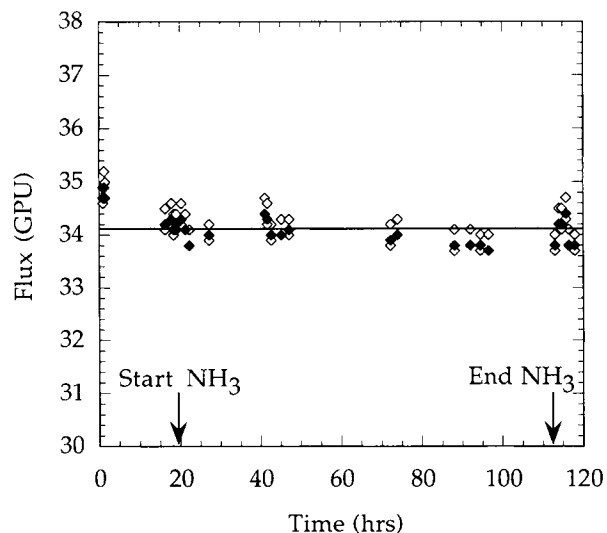

Figure 4 Stability of polyimide–ceramic composite at 250°C in the presence of butane–hydrogen–ammonia mixtures. Closed diamonds, data points. Open diamonds, error at each point.

Table V   Effect of Ammonia Exposure on the Hydrogen/Butane Selectivity of a Polyimide–Ceramic Composite Membrane at 250°C

Feed Conditions	Total Time on Line (h)	Mixed-Gas Selectivity[a]
Hydrogen/butane	10	> 260
Hydrogen/butane/NH_3	30	223
Hydrogen/butane/NH_3	50	260
Hydrogen/butane/NH_3	70	222
Hydrogen/butane	80	243

[a] Selectivity = (hydrogen$_{permeate}$/butane$_{permeate}$)/(hydrogen$_{feed}$/butane$_{feed}$). Stage cut ≈ 0.90.

observed in the presence of hydrogen, nitrogen, butane, butene, hydrogen sulfide, or ammonia. However, exposure to oxygen, even at moderate temperatures, resulted in degradation of the polymer structure and the formation of defects in thin layers of the material.

Based on these results, membranes utilizing 6FDA-IPDA polyimide as the separating layer appear to be sufficiently stable for use in high temperature petrochemical separations.

NOMENCLATURE

A area of the membrane (cm^2)

l effective membrane layer thickness (cm)

P permeability coefficient of the membrane material for the given penetrant [cm^3(STP) cm]/(s cm^2 cmHg)]

Q permeation rate (cm^3/s)

$\alpha_{A/B}$ selectivity of membrane for separation of A from B (unitless)

Δp partial pressure driving force across the membrane (cm Hg)

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