



Ultra-thin MFI membranes for removal of C₃₊ hydrocarbons from methane

Liang Yu*, Mattias Grahn, Jonas Hedlund

Chemical Technology, Luleå University of Technology, SE-971 87 Luleå, Sweden

ARTICLE INFO

Keywords:

MFI zeolite membrane
Natural gas upgrading
C₃₊ removal
Propane
Butane

ABSTRACT

The removal of propane and heavier hydrocarbons (C₃₊) from natural gas is an important part of natural gas upgrading. In the present work, ultra-thin MFI zeolite membranes with a thickness of 400 nm and an estimated Si/Al ratio of 152 were evaluated for separation of C₃H₈ and *n*-C₄H₁₀ from binary and ternary mixtures with CH₄. The membranes were selective towards the heavier hydrocarbons and showed high permeance at all investigated temperatures. At room temperature, the *n*-C₄H₁₀/CH₄ separation selectivity was 25, coupled with an *n*-C₄H₁₀ permeance of $31 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for a 10/90 *n*-C₄H₁₀/CH₄ binary feed mixture. As the temperature was decreased to 281 K, the separation selectivity increased to as high as 55 with an *n*-C₄H₁₀ permeance of $25 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The separation selectivities for a 10/90 C₃H₈/CH₄ binary mixture were 9.5 and 19, with C₃H₈ permeances as high as 54 and $37 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 297 and 271 K, respectively. The higher selectivities observed for *n*-C₄H₁₀ containing mixtures was ascribed to stronger adsorption of *n*-C₄H₁₀ than C₃H₈ in MFI, thus resulting in higher adsorption selectivities of the *n*-C₄H₁₀ containing mixtures over CH₄. For a 10/10/80 *n*-C₄H₁₀/C₃H₈/CH₄ ternary mixture, the highest sum selectivity of (*n*-C₄H₁₀ + C₃H₈)/CH₄ was 48 and the corresponding sum permeance of (*n*-C₄H₁₀ + C₃H₈) was $26 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 283 K, which were similar to the separation results of *n*-C₄H₁₀/CH₄ binary mixture at the same conditions. The *n*-C₄H₁₀/CH₄ and C₃H₈/CH₄ separation selectivities from the ternary mixture were of course lower, but still as high as 32 and 16 at 283 K, with *n*-C₄H₁₀ and C₃H₈ permeances of 17 and $8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively. The results show that ultra-thin MFI zeolite membranes are promising candidates for separation of C₃₊ hydrocarbons from natural gas.

1. Introduction

Natural gas is a mixture of hydrocarbons with CH₄ as the main species, typically constituting 75–90% of the raw gas [1,2]. Purified natural gas is of great importance not only as a source of energy with reduced emissions of CO₂ upon combustion as compared to coal and oil but also as a raw material for the chemical industry. It may be classified as “wet” or “dry” natural gas depending on if it is associated with crude oil (wet) or found in reservoirs in which no oil is present (dry). Dry natural gas only contains small amount of condensable hydrocarbons, e.g. *n*-C₄H₁₀ < 1% and C₃H₈ < 2% at ambient temperature, whereas in wet natural gas, the amount of *n*-C₄H₁₀ and C₃H₈ could reach 11% and 20%, respectively, at ambient temperature [3]. There are many reasons for removing the heavier hydrocarbons from natural gas e.g. to reduce soot and coke formation if the gas is used as fuel or to avoid problems with condensing liquids if the gas is to be compressed and transported in pipelines. Typical U.S. natural gas pipeline specifications are a C₃₊ content corresponding to between 950 and 1050 Btu/scf (British thermal unit/standard cubic foot) and a dew point lower than −20 °C

[2], which indicates the maximum C₃₊ content of 4.5% at ambient conditions. In addition, removal of heavy hydrocarbons from natural gas will increase the methane number, which is the natural gas counterpart of the octane number. It is an important quality parameter of natural gas transportation fuel [4]. Consequently, almost all natural gas requires some upgrading and considering the vast amount of natural gas produced in the world, natural gas processing is by far the largest industrial gas separation process.

Membrane separation is, in general, considered as a very energy efficient process and has been pointed out as a key technology to reduce energy consumption in the chemical industry. Polymer membranes have been used for upgrading of natural gas for decades, in particular for CO₂ removal [1]. Polymer membranes are also used for removal of C₃₊ hydrocarbons although the feasibility is limited due to rather low permeance and stability [2]. For removal of C₃₊ hydrocarbons from natural gas, different polymeric membranes have been investigated, for instance poly(1-trimethylsilyl-1-propyne) (PTMSP) exhibits the highest mixed-gas C₃₊ permeability coupled with the highest C₃₊/methane selectivity of all known polymers [4]. For separation of a binary 2/98 *n*-

* Corresponding author.

E-mail address: liang.yu@ltu.se (L. Yu).

C₄H₁₀/CH₄ mixture, a separation selectivity of 30 and a *n*-C₄H₁₀ permeance of as high as $6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ at room temperature and 16 bar pressure difference across the membrane has been reported [5]. Because of its outstanding mixed-gas separation properties, PTMSP was previously considered to be a promising membrane material for C₃+/methane separation. However, PTMSP has low solvent resistance and is consequently soluble in a wide range of organic solvents. Furthermore, the permeability of PTMSP to gases and vapours decreases over time as a consequence of physical aging, and this polymer membrane can therefore not be used in industrial applications [6,7]. The commercially used polymeric membranes e.g. polysulfone, PDMS etc. have much better physical aging resistance, but display separation selectivities of only 0.6–7, and a C₃+ permeance lower than $0.5 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ at room temperature [8]. Low permeance results in large membrane area needed to process a certain gas flow, whereas low selectivity necessitate multi-stage processes to minimize CH₄ loss, and both of these factors result in an expensive upgrading process. The low solvent stability is also an issue for commercial polymeric membranes and therefore more robust membranes should be developed. Zeolite membranes are considered especially attractive due to the unique properties of zeolites being inorganic crystalline aluminosilicates with well-defined pore size and high chemical and mechanical stability. Zeolite MFI has a pore diameter of ca. 0.55 nm, which is slightly larger than linear hydrocarbons such as *n*-alkanes. Consequently, MFI membranes have been widely explored for separation of different gas mixtures of hydrocarbons [9–12]. Santamaría et al., reported a highest *n*-C₄H₁₀/CH₄ selectivity of 31.5 at 25 °C, for silicalite-1 membranes, but the overall permeance was rather low, e.g. the permeance for C₂H₆ was lower than $1.0 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ [13]. Furthermore, most reports consider relatively thick MFI films, and the reported permeances are thereby low, comparable to polymeric membranes. Since ceramic zeolite membranes will be much more expensive than polymeric membranes per membrane area, zeolite membranes must display much higher permeance than polymeric membranes to be competitive [14].

Ultra-thin (500 nm) MFI zeolite membranes with high permeance have been developed in our group [15]. These membranes have been evaluated during 15 years for many separations, and of particular interest for the present work is our previous work on *n*/i-C₄H₁₀ separations [15] and olefin/nitrogen separations [16]. We have reported an *n*/i-C₄H₁₀ separation factor of 9 and an *n*-C₄H₁₀ permeance of $9.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at room temperature for a 500 nm film [15]. More recently, other groups have also reported very thin MFI membranes. MFI zeolite membranes with the thickness of less than 1 μm have been developed, which are promising advances for their commercial viability [17–19]. The thinnest membranes have been prepared using nanosheets as seeds, which results in films comprising b-oriented crystals [18]. The membranes had thicknesses of 100–250 nm and 250 nm ~ 1 μm, displaying a good *n*-butane/iso-butane selectivity and an extremely high *p*-xylene/*o*-xylene separation selectivity, respectively. In the present work, we evaluated our ultra-thin MFI membranes for removal of *n*-C₄H₁₀ and C₃H₈ from CH₄ for the first time. The separations were performed at different temperatures for binary C₃H₈/CH₄ and *n*-C₄H₁₀/CH₄ mixtures, and also for a *n*-C₄H₁₀/C₃H₈/CH₄ ternary mixture to identify suitable separation conditions.

2. Experimental

2.1. Membrane preparation and characterization

Porous graded α-alumina discs (Fraunhofer IKTS, Germany) with a diameter of 25 mm were used as supports. The top layer of the support is 30 μm thick with a pore size of 100 nm, and the base layer is 3 mm thick with a pore size of 3 μm. The membranes were prepared as described in a patent application [20]. Briefly, a dispersion of 50 nm silicalite-1 crystals was used for obtaining a monolayer of seed crystals on

top of the support. After seeding, the MFI zeolite films were grown in a synthesis mixture with a molar composition of 3TPAOH:25-SiO₂:1450H₂O:100EtOH in a plastic tube kept in an oil bath at 88 °C for 55 h under reflux. After synthesis, the membranes were rinsed in a 0.1 M NH₃ solution overnight and then calcined at 500 °C for 6 h at a heating rate of 0.2 °C min⁻¹ and a cooling rate of 0.3 °C min⁻¹.

The membranes were characterized using *n*-hexane/helium adsorption-branch permoporometry [21] in order to estimate the amount of flow-through defects. For this purpose, the membranes were mounted in a stainless steel cell sealed with graphite gaskets (Eriks, the Netherlands). A detailed description of the experimental and data evaluation procedures for permoporometry is given in previous work [22]. Scanning electron microscopy (SEM, FEI Magellan 400 field emission XHR-SEM) was used to investigate the morphology of the membranes. The Si/Al ratio of the zeolite film was estimated by energy dispersive spectroscopy (EDS) as described in detail in our previous report [23]. We showed that the Cs concentration in Cs-exchanged ZSM-5 crystals is equal to the Al concentration, and consequently, the Al concentration in ZSM-5 zeolite can be accurately estimated by ion-exchanging the sample to Cs+ form. The ion exchange was carried out in a 0.1 M Cesium Chloride (p.a., Merck) solution at 100 °C and reflux at atmospheric pressure for 1 h. The membranes were thoroughly rinsed with deionized water. The above procedure was repeated three times. The ion-exchanged membrane was coated with carbon before the Cs concentration was measurement by EDS using an accelerating voltage of 20 kV. Since Cs is much heavier than Al, the detection limit is improved and, in addition, this method is not influenced by any Al-signal from the alumina support.

2.2. Separation experiments

Prior to each separation measurement with a new gas mixture, the membranes were dried for 6 h at 300 °C under a flow of helium with a heating rate of 1 °C min⁻¹ followed by natural cooling. A Wicke-Kallenbach cell was used and the temperature inside the cell was monitored by a type K thermocouple. Separation experiments commenced when the cell had cooled to 323 K and sub-ambient membrane temperatures were achieved by placing the membrane cell in thermostated silicone oil. The desired feed flow rate was achieved by using needle valves and monitoring the flow rate by calibrated rotary flow meters (Brooks instrument, SHO-RATE, USA). The feed pressure was controlled by a backpressure regulator on the retentate line. The pressure on both sides of the membrane was monitored by pressure gauges. The permeate was kept at atmospheric pressure and no sweep gas was used. The permeate flow rate was measured using a drumtype gas meter (Ritter Apparatebau GmbH), and the composition of feed and permeate streams was analysed using a Micro GC (490 Micro GC, Agilent) connected online. A 10/90 *n*-C₄H₁₀/CH₄ binary mixture was fed to the membrane at a pressure of 7 bar at a flow rate of 5 l min⁻¹. For separation of the 10/90 C₃H₈/CH₄ binary mixture, the mixture was fed to the membrane at a total pressure of 9 bar and a flow rate of 10 l min⁻¹. For separation of the 10/10/90 *n*-C₄H₁₀/C₃H₈/CH₄ ternary mixture, the mixture was fed to the membrane at a total pressure of 9 bar and a flow rate of 5 l min⁻¹. The gas mixtures were purchased from AGA gas company with purities of methane and heavier hydrocarbons of > 99.9995% and > 99.95%, respectively.

Permeance, π (mol m⁻² s⁻¹ Pa⁻¹) and separation selectivity, α , were used to describe the separation performance of the membrane. The permeance π_i for component *i* is defined by:

$$\pi_i = \frac{F_i}{A \Delta P_i} \quad (1)$$

where F_i (mol s⁻¹) is the permeate molar flow rate of component *i*, *A* (m²) is the membrane area and ΔP_i (Pa) is the partial pressure difference of component *i* through the membrane.

The separation selectivity $\alpha_{i/j}$ is defined as the ratio of the

Download English Version:

<https://daneshyari.com/en/article/7020102>

Download Persian Version:

<https://daneshyari.com/article/7020102>

[Daneshyari.com](https://daneshyari.com)