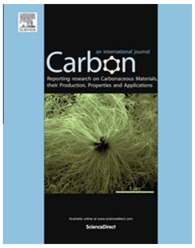
Available at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/carbon



A new carbon molecular sieve for propylene/propane separations

Junqiang Liu *, *Yujun Liu, Defne Kayrak Talay, Edward Calverley, Mark Brayden, Marcos Martinez*

The Dow Chemical Company, Midland, MI 48674, United States

ARTICLE INFO

Article history:
Received 12 November 2014
Accepted 21 December 2014
Available online 29 December 2014

ABSTRACT

A new carbon molecular sieve (CMS) with a propylene/propane separation factor of approximately 27 was synthesized by a facile pyrolysis process from a gel-type strong acid cation exchange resin. The micropore shrinkage process during pyrolysis was investigated using a new high throughput adsorption technique with 48 parallel cells. This significantly reduced the characterization time. The ratio of propylene/propane adsorption rate in the CMS adsorbent changes from 1 to more than 150 when the final pyrolysis temperature changes from 550 to 1000 °C. The best performing CMS pyrolyzed at 850 °C was further characterized using a gravimetric adsorption method. The propylene and propane diffusivities are 1.0×10^{-9} and 1.1×10^{-11} $cm^2\ s^{-1}$ at 100 kPa and 90 °C. The high propylene/propane diffusivity ratio of 90 is similar to that in zeolite 4A, while the propylene diffusivity was more than 30 times higher than that in zeolite 4A. An effluent of 90 mol% propylene was obtained from a feed of 25 mol% propylene during adsorption/desorption tests using the CMS adsorbent pyrolyzed at 850 °C in a fixed-bed configuration. The new CMS adsorbent is a promising candidate for industrial scale propylene/propane separations.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The separation of propylene from propane is currently dominated by distillation. Due to the close boiling points (−47.6 °C for propylene, −42.2 °C for propane), the purification process is very capital and energy intensive.

Several excellent review papers have been given on alternative separation methods including membrane [1], absorption [2], and adsorption [3], and their technical challenges. The use of π-complexation to selectively remove/transport olefin molecules has been investigated in all of these alternative processes [2–5]. However, the stability of the π-complexing species (Ag^+, Cu^+, etc.) has been a concern in the practical olefin/paraffin streams [2,6]. Separations based on size sieving mechanism on the other hand do not suffer from such instability issues. The kinetic diameter difference of propylene (4.0 Å) and propane (4.3 Å) is larger than that of oxygen (3.46 Å) and nitrogen (3.64 Å). It is therefore speculated the size-sieving based separation is more applicable to propylene/propane separation than the oxygen/nitrogen separation. The latter separation has been done commercially using a carbon molecular sieve (CMS) adsorbent since the 1970s [7]. The most important factor of an effective adsorbent is the propylene/propane selectivity, which is governed by the adsorbent pore size. Other parameters such as capacity, adsorption rate, and regenerability also have to be considered [8].

Small pore zeolites and Metal Organic Frameworks (MOFs) can separate propylene from propane based on their relative

---

* *Corresponding author.*
E-mail address: jliu7@dow.com (J. Liu).

http://dx.doi.org/10.1016/j.carbon.2014.12.089

0008-6223/© 2014 Elsevier Ltd. All rights reserved.

difference in diffusion rates into the micropores. A propylene/propane diffusivity ratio of 5.5 has been found in ZIF-8. However, the practical exploitation of the different diffusion rates or the molecular sieve effect seems to be complicated for MOFs because of their non-constant pore size [9]. Zeolite 4A showed excellent propylene/propane selectivity, but the activation requires 400 °C heating to remove the pre-adsorbed water due to the hydrophilic nature of the aluminosilicate structure. The use of such extreme activation temperature hurts the practicality of such molecular sieve adsorbents [10]. Several other 8-membered ring zeolites, such as Si-CHA and DDR, have high propylene/propane kinetic selectivity of more than 10,000. However, the propylene diffusivities are very low, i.e., in the range of 1×10^{-12}–1×10^{-11} $cm^2\ s^{-1}$. A very small zeolite crystal size must be used to obtain a reasonable adsorption/desorption time [11]. Aluminophosphate ALPO34 is reported to have a much higher propylene diffusivity of 5×10^{-10} $cm^2\ s^{-1}$ and workable propylene/propane selectivity above 50 [11]. However, the long term instability of ALPO34 is a concern for any large scale application [12].

CMS adsorbents with molecular sieving pores have been widely used commercially for oxygen/nitrogen separations [13]. The commercial CMS adsorbents are derived from coal or plant sources to reduce the cost of the adsorbent. The pore size in the commercial CMS adsorbent is controlled by the deposition of different molecules in a chemical vapor deposition (CVD) process [14]. For instance, benzene is used to deposit onto the opening of the slit carbon pore to reduce its size until the pore size is about the width of the benzene molecule (3.7 Å). The CMS formed through this process is used for industrial O_2/N_2 separations [14]. No CMS adsorbent suitable for propylene/propane separation has been reported based on the traditional CVD process. Two features of gas separation using CMS adsorbents should be noted at the outset.

1. The ability of these CMS materials to separate small molecule gases is driven primarily by kinetic phenomena – i.e., the relative rates at which the subject molecules can penetrate the pore structures – rather than by thermodynamic (i.e., equilibrium) factors.
2. Carbons produced by pyrolysis of naturally occurring or polymeric organic materials are amorphous, lacking regular structure and characterized by a complex network of generally slit shaped pores. The rates of adsorbate uptake into the primary particles are affected by the size distribution and the connectivity of the pore structure. This means that pore sizes estimated by equilibrium adsorption measurements will be only approximate indicators of when good separation selectivity can be expected. This is because such static measurements are not able to completely account for the combination of pore sizes, connectivity and tortuosity that determine adsorption kinetics.

The carbon pore size in many synthetic polymer-based carbons can be tuned via pyrolysis intensity [15]. For instance, the same commercial Matrimid® polyimide polymer has been pyrolyzed at 650 °C to make carbon membranes suitable for ethylene (3.9 Å)/ethane (4.1 Å) separations [16]. A higher pyrolysis temperature of 800 °C is suitable to make carbon membranes for nitrogen (3.64 Å)/methane (3.8 Å) separations [17]. Many other studies have been done to make CMS membranes for various gas separations using different precursors, such as polyimide [18,19], phenolic resin [20,21], polyfurfural alcohol [22,23], and other precursors. Several orders of magnitude higher permeability than that in the incumbent polymeric membranes has been found in the CMS membranes. However, for practical applications, thin CMS films (submicron ideally) must be made in order to achieve the high permeance. The incumbent polymeric membranes exhibit high permeance because their effective film thicknesses are only a few hundred nanometers. Obstacles exist to make such thin film CMS membranes because thin films must be made at the polymer precursor stage and then survive the high temperature pyrolysis process [24]. Furthermore, forming thin defect-free film membranes of fragile CMS materials is much more challenging than from flexible polymeric materials.

The synthetic polymers used for CMS membranes mentioned above can also be made into CMS adsorbents for Pressure Swing Adsorption (PSA) separations. The barriers to implementation of this technology in an industrial setting are lower as evidenced by the existence of commercial air separations based on CMS adsorbents. Thus, while CMS membranes are relevant for the propane/propylene separation studied in the present work, PSA for separations at modest industrial scale is a potentially viable short term opportunity.

Low cost precursors must be used to make industrially viable CMS adsorbents. Cation exchange resin, which is made of commodity polystyrene copolymer beads and sulfuric acid, is one of the inexpensive carbon forming precursors. The cost is typically at least one order of magnitude lower than those of engineering thermoplastics such as polyimide. Carbon derived from sulfonated polystyrene (cation exchange resin) has been studied since the 1980s [25–27]. However, these carbons were derived from macroporous resins and had polydispersed micropores and macropores. The Dow Chemical Company has one such product named Ambersorb™ for water treatment applications [28–30]. The separation is based on the higher affinity of other chemical species than water (similar to activated carbon) without molecular sieving properties. Therefore, it is fundamentally different from what is reported in the present work. Miura pyrolyzed gel-type cation-exchange resins exchanged with several kinds of cations to make microporous carbons [31,32]. It was found that carbon materials prepared from the resins with divalent or trivalent cations had larger micropore volume while those prepared from resins with univalent cations (including hydrogen) lost most of their micropores as well as their spherical macrostructure during a 900 °C pyrolysis. The loss of micropore volume may have been due to the limitation of their characterization method. Specifically, the slow diffusion of adsorbate into their large 200 μm carbon beads may have been misinterpreted as low adsorption capacity (therefore low micropore volume).

We have found very different results from those reported by Miura, in that our hydrogen-exchanged resins retained their spherical shape and significant micropore volume upon pyrolysis. Furthermore, CMS adsorbents with a very high

Download English Version:

https://daneshyari.com/en/article/1413534

Download Persian Version:

https://daneshyari.com/article/1413534

Daneshyari.com