



High throughput development of one carbon molecular sieve for many gas separations



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ABSTRACT

A set of CMS adsorbents was synthesized by pyrolyzing gel-type cation exchange resins (IERs) based on sulfonated poly(styrene-co-divinylbenzene). Fifteen different materials were synthesized following a design of experiments (DOE) that included variations on four factors. These factors were divinylbenzene (DVB) content, plus three factors associated with pyrolysis (peak temperature, hold time, and temperature ramp rate). Results revealed that the peak temperature has a significant impact on the micropore volume and the effective pore size of the resultant CMS adsorbents, but the other three input variables have very little impact. High throughput single gas adsorption was conducted on the fifteen CMS adsorbents using nine probe gas molecules: CO₂ (kinetic diameter 3.3 Å), N₂ (3.64 Å), CH₄ (3.8 Å), C₂H₄ (3.9 Å), C₃H₆ (4.0 Å), C₂H₆ (4.1 Å), C₃H₈ (4.3 Å), *i*-C₄H₁₀ (5.0 Å), SF₆ (5.5 Å). Based on gas pair selectivities calculated from the single gas adsorption data, pyrolysis process boundaries were defined to make suitable CMS adsorbents with effective micropore size in the range of 3.5–4.6 Å. Based on the high throughput findings, four additional CMS adsorbents were produced for the industrially significant separations: C₃H₆/C₃H₈, C₂H₄/C₂H₆, N₂/CH₄, and CO₂/N₂. Breakthrough performance of the four target gas pairs was characterized in a packed bed configuration using binary gas mixtures of the four target gas pairs. The four CMS adsorbents exhibited high separation factors, 43 for C₃H₆/C₃H₈, 10 for C₂H₄/C₂H₆, 9 for N₂/CH₄, and 12 for CO₂/N₂, illustrating the validity of the high throughput results.

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1. Introduction

Carbon molecular sieve (CMS) adsorbents have been widely used commercially for oxygen/nitrogen separations [1]. 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 [2]. The micropore size in the commercial CMS adsorbent is discrete and is particularly suitable for the oxygen/nitrogen separation. There are potentially more industrial gas separation applications if a carbon molecular sieve with proper pore size can be made.

Propylene/propane separation is claimed to be the most energy intensive gas separation [3]. The relative volatility of the two molecules is only about 1.1, which causes high energy consumption for the separation process by distillation. For separation by adsorption, a highly selective adsorbent is needed in order to reach the high purity requirement of propylene (typically > 99%). One study suggests a hybrid of PSA (pressure swing adsorption) and distillation,

where only a moderately selective adsorbent is needed [4]. Small pore zeolites and metal organic frameworks (MOFs) can separate propylene from propane based on their relative difference in diffusivity rates into the micropores. A propylene/propane diffusivity ratio of 5.5 has been found in zeolitic imidazolate framework-8 (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 varying pore size at different hydrocarbon pressures [5]. Zeolite 4A showed excellent propylene/propane selectivity, but the activation requires 400 °C heating to remove the pre-adsorbed water due to its hydrophilic aluminosilicate structure. The use of such extreme activation temperature hurts the practicality of such molecular sieve adsorbents [6]. 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} to 1×10^{-11} cm²/s. A very small zeolite crystal size must be used to obtain a reasonable adsorption/desorption time [7]. Zeolite ALPO34 is reported to have a much higher propylene diffusivity of 5×10^{-10} cm²/s and workable propylene/propane selectivity above 50 [7]. However, the long term instability of ALPO34 is a concern for any large scale application [8].

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Similar to the propylene/propane separation, ethylene/ethane separation is also very energy intensive using the traditional distillation method. For instance, the distillation is performed at around $-25\text{ }^{\circ}\text{C}$ and 320 psig in a column containing over 100 trays with a high reflux. Similar to other olefin/paraffin separations, chemisorption adsorbents using Ag^+ ions have been investigated [9–11]. However, no molecular sieve adsorbent has been reported to separate ethylene/ethane based on a size sieving mechanism because of the extremely small difference in molecular size.

For the production of fuel grade methane, nitrogen needs to be removed to a certain level (less than 3%) in many streams, such as coal bed methane, biogas methane, and some natural gas streams. Adsorbent technology is particularly suitable for these N_2 removal/purification applications if one can design adsorbents that selectively remove nitrogen from methane. A molecular sieving adsorbent has been suggested, but the only adsorbents that have shown some success so far are the Engelhard (now BASF) Molecular Gate™ adsorbents [12]. The adsorbent is a titanosilicate structure (ETS-4) that preferentially adsorbs nitrogen over methane on an equilibrium basis. The limitation of the ETS-4 adsorbent is its change of structure when hydrated [13].

The carbon pore size in many synthetic polymer-based carbons can be tuned via pyrolysis intensity [14,15] for these different gas separations. For instance, the same commercial Matrimid® polyimide polymer has been pyrolyzed at $650\text{ }^{\circ}\text{C}$ to make carbon membrane suitable for ethylene (3.9 \AA)/ethane (4.1 \AA) separations [16], and a higher pyrolysis temperature of $800\text{ }^{\circ}\text{C}$ to make carbon membranes for nitrogen (3.64 \AA)/methane (3.8 \AA) separations [17]. Many other works 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) has to be made in order to achieve high permeance to compete with the incumbent polymeric membranes, which has an effective film thickness of only a few hundred nanometers. Obstacles exist to make such thin film CMS membranes, such as precursors form thin film well melt and form thick CMS films [24] and precursors do not melt also do not form thin film well [22,23]. Furthermore, forming thin film membrane of fragile CMS materials defect-free is much more challenging than that from flexible polymeric materials.

The synthetic polymers used for CMS membranes mentioned above can also be made into CMS adsorbents used in Pressure Swing Adsorption (PSA) separation processes. The adsorbent typically requires a primary particle size (powder to make adsorbent pellet) on the scale of several microns or larger (depend on the diffusion rates) and has much less defectiveness concern during the production process. A sacrifice on the process may be made, adopting a discontinuous PSA process rather than a continuous membrane process, in order to achieve an industrially feasible separation media, an adsorbent pellet rather than a defect free membrane. That might be the reason why CMS adsorbent has been commercialized since the 1970s for air separation, while the CMS membrane is still in development.

Low cost precursors have to 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 by researchers in the previous Rohm & Haas Company [25–27]. However, these carbons were derived from macroporous resins and were made as one type of activated carbon. The Dow

Chemical Company has one such product named Ambersorb™ (developed by the previous Rohm & Haas Company) for water treatment applications [28–30]. The separation is based on the higher chemical affinity of other species than water (similar to activated carbon without molecular sieving properties). 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 have larger micropore volume while those prepared from resins with univalent cations (including hydrogen cation) lost most of their micropores and the spherical macrostructure at $900\text{ }^{\circ}\text{C}$ pyrolysis. The loss of micropore volume may be due to the limitation of their characterization method, in which a slow diffusion in their huge $200\text{ }\mu\text{m}$ carbon beads may be misinterpreted as low adsorption (therefore low micropore volume).

In this report, we found quite contrary result to Miura's that not only the carbon beads from the pyrolysis of hydrogen from cation exchange resin maintain a perfect spherical shape, but also a large amount of micropores for adsorption. Here we report a systematic investigation aimed at determining the dependence of effective pore size of IER based CMS on variations in precursor chemistry as well as pyrolysis process variables. This work involved the synthesis and high-throughput characterization of fifteen different IER CMS adsorbents following a design of experiment (DOE). This set of IER CMS adsorbents gave micropore sizes ranging from 3.5 to 4.6 \AA . Based on the DOE study, four additional CMS adsorbents were prepared that exhibited high separation factors, 43 for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$, 10 for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$, 9 for N_2/CH_4 , and 12 for CO_2/N_2 , illustrating the validity of the high throughput results.

2. Experimental

2.1. Experimental design

Experimental design was constructed following a pseudo-hyper-Graeco-Latin square (p-HGLS) design using the JMP Statistical Discovery computer program (<http://www.jmp.com/>). The p-HGLS DOE included 15 experiments evenly distributed over the four factors, as shown in Table 1. This design included 4 input variables. They were (i) peak temperature at which the pyrolysis was carried out (from 700 to $1200\text{ }^{\circ}\text{C}$ at $125\text{ }^{\circ}\text{C}$ intervals), (ii) hold time at the peak temperature (0, 30 and 60 min.), (iii) ramp rate to the peak temperature (2, 6 and $10\text{ }^{\circ}\text{C}/\text{min}$), and (iv) DVB cross-linker content (2, 4 and 8 wt%). For temperature, the DOE list includes three experiments for each of the five levels. For the other factors the list includes five experiments at each of the three levels.

Table 1
DOE design.

Pyrolysis severity	Temperature [$^{\circ}\text{C}$]	Hold time [min]	Ramp rate [$^{\circ}\text{C}/\text{min}$]	DVB [wt%]
1	700	0	2	2
2	700	30	10	8
3	700	60	6	4
4	825	0	6	8
5	825	30	10	2
6	825	60	2	4
7	950	0	10	8
8	950	30	6	4
9	950	60	2	2
10	1075	0	6	2
11	1075	30	2	4
12	1075	60	10	8
13	1200	0	10	4
14	1200	30	2	8
15	1200	60	6	2

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