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Carbon molecular sieves from hardwood carbon pellets. The influence of carbonization temperature in gas separation properties

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Abstract

The influence of carbonization temperature in the preparation of hardwood carbon molecular sieves (CMS) has been studied. The textural characterization of the obtained materials included adsorption isotherms of CO_2, C_2H_6 and n-C_4H_{10} to obtain the micropore size distribution. Adsorption kinetics of CH_4, CO_2, C_3H_6 and C_3H_8 were measured in all materials to determine their behavior as molecular sieves. Results confirm that the carbonization temperature of this hardwood has a very significant effect on the resulting CMS separation properties. The increase in the wood's carbonization temperature reduced the CMS micropore size distribution. Consequently, high carbonization temperatures (1000 °C) are required to obtain good CH_4/CO_2 separation, while a low carbonization temperature (700 °C) is best for C_3H_6/C_3H_8 separation. The differences in separation properties of these materials could be explained by a partial blocking of the micropore entrance produced by disorganized carbon migrating from the internal structure (chars) and by the additional binder used to prepare the CMS.

Keywords: Carbon molecular sieves; CO_2/CH_4 separation; C_3H_6/C_3H_8 separation; Charcoal

1. Introduction

Chemical process industry has become increasingly interested in the development of low cost gas separation processes and gas separation technology is quite closely connected to improved molecular sieving materials. Molecular sieves can be defined as materials with discrete pore structures that can discriminate between molecules based on their size [1]. For many years, molecular sieves such as zeolites and carbon molecular sieves have been successfully used as adsorbents in the field of gas separations [2].

Carbon molecular sieves are a special class of activated carbons which may exhibit advantages over zeolite molecular sieves such as higher hydrophobicity, higher resistance to both alkaline and acid media, and thermal stability at high temperatures under non-oxidizing atmosphere [3]. Zeolites are crystalline aluminosilicates with cavities and cylindrical-shaped pores [4]. Matter transfer into the zeolite inner structure is limited by the diameter of the entrance at the cavity or by the pore diameter. Unlike zeolites, active carbons are formed by disorganized graphitic-like planes [5,6] with,

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therefore, slit-shaped pores and variable pore size distributions.

The micropore structure of such carbons is unique, since the slit-like apertures or the constrictions of the micropores are of a size similar to the molecular dimensions of the adsorbing species. For example, experimental evidence has shown the preferential adsorption of flat molecular probes versus the non-sorption of spherical molecular probes of similar dimensions [7]. Indeed, differences in the dimensions and shape of the adsorbing molecules produce differences in the adsorption kinetics, originating the corresponding selectivity of the CMS. This kinetic feature makes CMS capable of separating species, even when the equilibrium capacity of the carbon is similar for both of them. CMS's exhibit preferential adsorption for species whose molecular size is smaller than the micropore entrance. In gas separation, molecules smaller than the size of the micropore constrictions rapidly diffuse through them into the associated micropore volume. On the other hand, access for a larger molecule to the associated volume is denied due to the constrictions. A small change in the effective size of the constriction can considerably affect the diffusion rate of an adsorbing gas molecule. In the case of CH_4/CO_2 separation, for example, these constrictions at the entrance of the micropores allow CO_2 to preferentially diffuse into the interior of the micropores, since the CO_2 molecule dimension is about 0.05 nm smaller than that of the CH_4. As a result, CO_2 is adsorbed faster onto the CMS while CH_4 preferentially remains in the gas phase.

CMS's can be prepared from a variety of precursors such as polymers, coconut shells, wood, bituminous carbon, etc. [8–11]. The porosity of the sieve greatly depends on the raw material and the sieve preparation procedure, which is not easily controllable. Carbonization temperature has been recognized as one of the most important preparation variables [12–15]; however, a systematic study of the carbonization process over a wide temperature range (600–1000 °C) and the analysis relating the results with the molecular sieving properties of the obtained material has not been reported in the consulted literature.

An earlier work [16] reporting the preparation of hardwood CMS pellets, described that high heating rates and a short activation time during the CMS pellet formation improved the separation properties for CO_2/CH_4. Furthermore, an increase in the carbonization temperatures from 830 °C to 870 °C also enhanced the selectivity for the CO_2/CH_4 separation.

This paper reports a systematic study of the influence of carbonization temperature, between 600 and 1100 °C, on the preparation of CMS pellets from Eucalyptus globulus. The textural properties of the CMS's and the corresponding chars are related to their selectivities in CH_4/CO_2 and C_3H_6/C_3H_8 separations.

2. Experimental

2.1. Preparation

The preparation of CMS pellets, previously reported [16], was similar to the one used by Miura et al. [10]. Chips of Eucalyptus globulus 5 cm in length were carbonized under nitrogen atmosphere for 2 h in a vertical furnace. A heating rate of 4 °C min^{-1} and different carbonization temperatures in the range 600–1100 °C were used. Once powdered, the chars were blended with a coal tar pitch and an organic solvent in a rotary evaporator, and dried at 110 °C to obtain an extrudable mixture. Subsequently, pellets were formed by extruding the mixture with a hydraulic press. Finally, the pellets were submitted to a short heat treatment under a flow of CO_2 in previously optimized conditions (11 °C min^{-1} as heating rate, 600 °C for 6 min) [16]. Cylindrical pellets of approximately 5 mm in length for 2 mm of diameter were obtained.

In this work chars are designated by a C followed by the carbonization temperature. Carbon molecular sieves are designed by the abbreviation CMS, followed by the carbonization temperature of the char used in their preparation.

2.2. Characterization

A thermobalance TGA/SDTA851 Mettler Toledo was used for thermogravimetric studies. Dynamic TGA studies were carried out at a linear heating rate of 10 °C min^{-1}, covering the temperature range from 25 to 1000 °C. The studies were carried out in an inert atmosphere of nitrogen and in a reactive atmosphere of carbon dioxide.

The hardness was estimated using a comparative method. A sample of material, between 10 and 20 mesh in size, was placed into a stainless steel cylinder containing 5 stainless steel balls of 5 mm in diameter and shacked for 90 s. The sample was then sieved, and hardness was taken as the percentage of material that retained a size over 20 mesh.

The micropore volume distribution was obtained from the adsorption isotherms of carbon dioxide, ethane and *n*-butane at 0 °C. The isotherms were obtained with a Micromeritics Gemini 2370 volumetric adsorption apparatus. From adsorption data, micropore volume was determined using the Dubinin–Radushkevich (DR) equation [17]. The minimum dimensions of such gas molecules are reported to be 0.33, 0.40 and 0.43 nm, respectively [4].

2.3. Adsorption kinetics

The adsorption kinetics of methane, carbon dioxide, propane and propylene on the prepared materials was