Journal of Colloid and Interface Science 394 (2013) 445–450

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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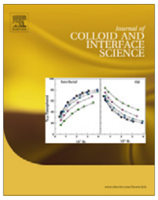

Adsorptive separation studies of ethane–methane and methane–nitrogen systems using mesoporous carbon

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ARTICLE INFO

Article history:
Received 15 September 2012
Accepted 8 December 2012
Available online 19 December 2012

Keywords:
Adsorption
Ethane
Methane
Nitrogen
Mesoporous carbon
Equilibrium selectivity
Isosteric heat of adsorption

ABSTRACT

Adsorptive separations of C_2H_6/CH_4 and CH_4/N_2 binary mixtures are of paramount importance from the energy and environmental points of view. A mesoporous carbon adsorbent was synthesized using a soft template method and characterized with TEM, TGA, and nitrogen adsorption/desorption. Adsorption equilibrium and kinetics of C_2H_6, CH_4, and N_2 on the mesoporous carbon adsorbent were determined at 278, 298, and 318 K and pressures up to 100 kPa. The adsorption capacities of C_2H_6 and CH_4 on the mesoporous carbon adsorbent at 298 K and 100 kPa are 2.20 mmol/g and 1.05 mmol/g, respectively. Both are significantly higher than those of many adsorbents including pillared clays and ETS-10 at a similar condition. The equilibrium selectivities of C_2H_6/CH_4 and CH_4/N_2 at 298 K are 19.6 and 5.8, respectively. It was observed that the adsorption of C_2H_6, CH_4, and N_2 gases on the carbon adsorbent was reversible with modest isosteric heats of adsorption, which implies that this carbon adsorbent can be easily regenerated in a cyclic adsorption process. These results suggest that the mesoporous carbon studied in this work is a promising alternative adsorbent for the separations of C_2H_6/CH_4 and CH_4/N_2 gas mixtures.

1. Introduction

It is well known that natural gas is an important source of energy. Approximately 25% of the worldwide energy supply comes from the natural gas in 2004 [1,2], and the consumption of the natural gas has been increasing in recent years (EIA report, 2010). Natural gas is composed primarily of methane (CH_4) with variable proportions of heavier hydrocarbons (C_{2+}) and other contaminants, CO_2, N_2, for instance. The presence of N_2 decreases the heating value of the natural gas, and the "pipeline quality methane" specification requires that the proportion of N_2 should be within 4%. About 14% of the natural gas reserves in the US cannot meet this requirement [3]. Therefore, separation of CH_4 and N_2 is demanded for the utilization of low quality natural gas.

Methane is one of the main components of greenhouse gases. The global warming potential (GWP) of CH_4 is much higher than that of CO_2 [4,5]. Landfill gas (LFG) significantly contributes to the emission of CH_4 [6,7]. N_2 concentration in the LFG is relatively high when the LFG is collected at pressures lower than atmospheric pressure in order to increase the CH_4 yield [6]. To reduce the CH_4 emission and upgrade the highly N_2-contaminated LFG, it is necessary to separate the N_2 and CH_4.

C_2H_6 is an important reactant for the synthesis of ethylene that is widely used to produce films, plastics, and etc. [8]. Separation of C_2H_6 and CH_4, the largest two components of raw natural gas, is industrially significant to obtain the C_2H_6. Meanwhile, C_2H_6 could be produced by the oxidative coupling of methane (OCM), a way to convert the largest component of natural gas (CH_4) to more valuable heavier hydrocarbons [9,10]. An efficient process for the separation of C_2H_6 from unreacted CH_4 will contribute to the oxidative coupling of methane process.

The separations of C_2H_6/CH_4 and CH_4/N_2 are carried out mostly by cryogenic distillation, which is a highly energy and cost intensive separation process, especially in small-scale application [2,8,11]. The adsorption-based separation process is a promising alternative technology to the cryogenic distillation, particularly for the case of small to medium volume of operations [11–13]. The pressure swing adsorption (PSA) has become a competitive gas separation technique due to its advantages of simple operation, low operating costs, high-energy efficiency, etc. [14–16]. It involves the selective adsorption at a high pressure and desorption (regeneration) at a relatively low pressure. To fulfill the separation in a PSA process, appropriate adsorbents with enough selectivity, adequate adsorption capacity, high thermal stability, and ease of synthesis and regeneration are needed.

A large number of studies have been carried out for the adsorptive separations of CH_4/N_2 [17–22] and C_2H_6/CH_4 [23–28] in recent years, and most of the reported studies have focused on activated carbon (AC), metal organic framework (MOF), clays, and titanosilicates. However, these adsorbents have several shortcomings. Saha et al. reported that MOF-177 exhibits a selectivity of 4 for the

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http://dx.doi.org/10.1016/j.jcis.2012.12.025

separation of CH_4/N_2 with a low CH_4 uptake capacity of ~0.6 mmol/g at 298 K and 100 kPa. The overall kinetic selectivity of CH_4/N_2 by carbon molecular sieve at 308 K was found to be as low as 1.9 [29]. It was found that the equilibrium selectivity of C_2H_6 over CH_4 at 298 K and adsorption capacity of C_2H_6 at 298 K and 100 kPa on the clays are below 6, and below 0.8 mmol/g, respectively [28,30]. ETS-4 and ETS-10 are attractive adsorbents for CH_4/N_2, C_2H_6/CH_4 separations in terms of equilibrium selectivity [8,19,27]. However, the synthesis processes of these zeolite adsorbents are time-consuming and complicated [20,31]. Therefore, adsorbents, which could be easily synthesized in a short term, with acceptable selectivities of CH_4/N_2 and C_2H_6/CH_4, and also with large corresponding CH_4 and C_2H_6 uptake capacities are greatly desired.

Recently, different kinds of mesoporous materials have been studied for adsorption and separation of gases [32–35,16]. The mesoPOFs have been reported as promising adsorbents for the separation of C_2H_6 from CH_4 [25]. Liu et al. [34] evaluated the SBA-15 for the separation of CO_2 and CH_4. MCM-41 has been tested for the separations of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 binary gas mixtures [35]. Mesoporous carbon materials synthesized by the soft template method are emerging as a novel class of adsorbents. They have received much attention due to their attractive properties, such as ease of synthesis, low cost, chemical inertness, large surface area, and tunable pore texture [36–39]. The main aim of this study is to explore the potential application of mesoporous carbon in adsorptive gas separations, in particular, the separations of CH_4/N_2 and C_2H_6/CH_4. Mesoporous carbon was synthesized via the soft template method and then characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and nitrogen adsorption and desorption isotherms at 77 K. Adsorption equilibrium and kinetics of N_2, CH_4, and C_2H_6 on the synthesized mesoporous carbon were determined and analyzed.

2. Experimental

2.1. Synthesis of mesoporous carbon

The mesoporous carbon studied in this work was synthesized by soft template method following the procedures reported by Zhao's group [40] with slightly modification. Typically, 1.6 g poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock copolymer Pluronic F127 (Sigma–Aldrich) was added to a solution of 32 g ethanol (99.9%, Sigma–Aldrich), 20 g deionized water, and 1 g of 0.2 M HCl. The mixture was heated to 40 °C under stirring. Then, 2.08 g tetraethyl orthosilicate (99+%, Sigma–Aldrich) and 5 g 20% pre-synthesized resins (see supporting information) were added to the mixture followed by stirring for 2 h at 40 °C. The mixture was poured into dishes to evaporate the ethanol and water. Then, it was thermo-polymerized at 100 °C for 24 h. Calcination at 350 1 °C for 5 h and 800 °C for 4 h was done under nitrogen atmosphere in a tubular furnace with a heating rate of °C/min. The mesoporous carbon was obtained after the removal of the silica by 4 M NaOH (98+%, Sigma–Aldrich) etching at 40 °C, filtration, washing thoroughly with copious deionized water, and drying at 50 °C.

2.2. Characterization of mesoporous carbon

The pore structure of the as-made mesoporous carbon was determined by transmission electron microscopy (TEM) images taken with Hitachi H-7650. Thermogravimetric analysis (TGA) was carried out on Pyris 1 TGA from room temperature to 950 °C under oxygen with a heating rate of 10 °C/min. By using Micromeritics ASAP 2020 adsorption instrument, the nitrogen adsorption and desorption isotherms on the sample were measured at 77 K. Before the adsorption measurement, the sample was degassed under a vacuum at 250 °C for over 12 h for the removal of guest molecules incorporated into the sample. The pore textural properties including the Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore size distribution were obtained from the nitrogen sorption isotherms by the Micromeritics ASAP 2020 built-in software.

2.3. Adsorption measurements

The adsorption equilibrium data of N_2, CH_4, and C_2H_6 on the mesoporous carbon were recorded via the Micromeritics ASAP 2020 adsorption instrument volumetrically at three temperatures (278, 298 and 318 K) and gas pressure up to 100 kPa. Ultrahigh purity grade N_2, CH_4, and C_2H_6 were used as received. The degas procedure was carried out under a vacuum at 250 °C for over 12 h before the adsorption measurement in order to remove the guest molecules.

During the measurement of the equilibrium adsorption data, the kinetic adsorption data were also collected. A certain adsorbate gas was first conducted in the adsorption unit at a designated dose. The adsorbate gas pressure was measured at designated intervals. Then, it was converted to uptake quantity as a function of time automatically, which gives the adsorption kinetics data. The gas uptake quantity at the terminal pressure was taken as the equilibrium adsorption capacity at that pressure.

3. Results and discussion

3.1. Physical properties

Fig. 1 shows the thermogravimetric analysis (TGA) curve of the mesoporous carbon in an oxygen atmosphere. As can be seen from the TGA plot, the silica component was completely removed from the carbon framework. The initial weight loss (~3.5%) before 400 °C is due to the loss of water trapped inside the pores of the sample. It can be concluded that the as-made mesoporous carbon is stable up to about 400 °C in an oxygen atmosphere, which is more stable than MOFs [41] and mesoPOFs adsorbents [25].

The mesoporous structure of the carbon sample synthesized in this work was confirmed by the TEM image, as shown in Fig. 2. Spherical pores with uniform diameters can be clearly observed. The pores are homogeneously distributed throughout the whole sample.

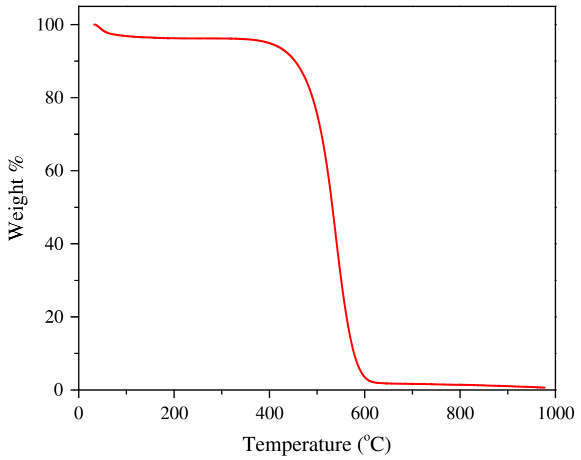

Fig. 1. Thermogravimetric analysis of the as-synthesized mesoporous carbon.