

Asphalt-derived high surface area activated porous carbons for the effective adsorption separation of ethane and ethylene



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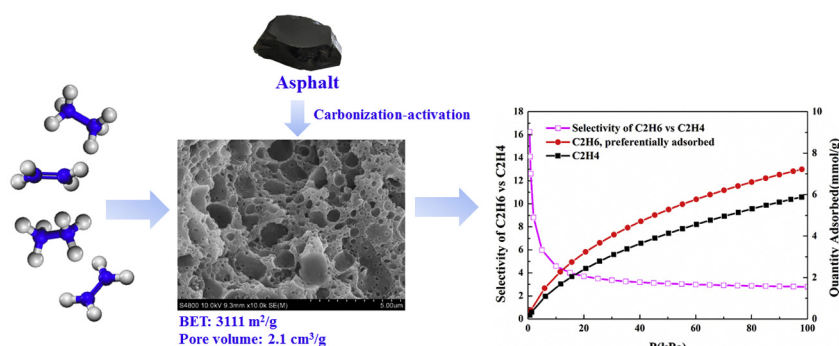
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HIGHLIGHTS

- A series of asphalt-based activated carbons (A-ACs) are successfully synthesized.
- A-ACs exhibit ultra-high BET area of 3111 m²/g and pore volume of 1.92 cm³/g.
- A-ACs are ethane-selective adsorbents with super high ethane uptake of 7.2 mmol/g at 25 °C and 100 kPa.
- Ethane/ethylene adsorption selectivity of A-ACs is up to 16.3 for the cracked gas mixture.

GRAPHICAL ABSTRACT



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ABSTRACT

We reported novel asphalt-based activated carbons (A-ACs) with high C₂H₆/C₂H₄ adsorption capacity and selectivity. A series of A-ACs were prepared by a one-step preparation method and characterized. The adsorption performances of A-ACs for ethane/ethylene were examined. Results showed that the sample A-ACs prepared at 800 °C and the KOH/asphalt ratio = 4 exhibited ultra-high BET area of 3111 m²/g and its pore volume reached 1.92 cm³/g. Their surface O and N contents gradually decreased with activation temperature or KOH/asphalt ratio at which A-ACs were prepared. More interestingly, A-ACs showed significantly preferential adsorption of C₂H₆ over C₂H₄. It could be ascribed to the stronger interaction of C₂H₆ with the surfaces of A-ACs by hydrogen bonds compared to C₂H₄, which were revealed by Density functional theory calculation. Its C₂H₆ adsorption capacity was up to 7.2 mmol/g at 100 kPa and 25 °C and its C₂H₆/C₂H₄ adsorption selectivity for typical cracked gas mixture (15:1 ethylene/ethane) was in the range of 3.2–16.3 at the pressure below 100 kPa, higher than the most reported ethane-adsorbents. Additionally, the isosteric heat of ethane and ethylene adsorption on A-ACs were lower than those on π -complexation adsorbents. Therefore, these excellent adsorption properties would make A-ACs as a type of promising adsorbents for adsorption separation of C₂H₆/C₂H₄.

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1. Introduction

Alkenes are the very important feedstocks used not only as raw materials in the manufacture of polymers, but also as intermedia for

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the synthesis of other organic chemicals. Alkenes are produced by hydrocarbon cracking. Global annual production of ethylene and propene exceeds 200 million tonnes (Sholl and Lively, 2016). Ethylene (C_2H_4) is the simplest alkene produced on the largest scale industrially (Sholl and Lively, 2016). During the production of high-purity ethylene, after removal of other contaminants, ethylene needs to be separated from ethane. Nowadays, the industrial separation of ethylene and ethane typically is performed in the high-pressure (23 bar) cryogenic distillation column with over 100 trays at temperatures as low as $-25\text{ }^\circ\text{C}$ (Tao et al., 2006; Eldridge, 1993), which is energy-intensive and expensive to operate, and accounts for 75–85% of the ethylene production costs (van Miltenburg et al., 2006). To save energy and to reduce the ethylene production cost, it is highly desired to develop new separation methods which can be operated effectively at ambient temperature and pressure (Sholl and Lively, 2016).

Adsorptive separation is considered as an energy-efficient alternative (Ruthven, 2000). An adsorbent is the core of adsorption technique. Bao et al. (2011) investigated the adsorption of ethane and ethylene on Mg-MOF-74. It was reported that Mg-MOF-74 displayed the characteristic of adsorbing ethylene preferentially, and its ethylene uptake was about 7.2 mmol/g at $25\text{ }^\circ\text{C}$ and 100 kPa, while the ethane uptake is about 6.5 mmol/g. Li et al. (2014) synthesized the Ag(I) functionalized porous aromatic framework (PAF-1- SO_3Ag), and reported that the introduction of π -complexation into a porous aromatic framework, affording significant increase in ethylene adsorption capacity and exceptionally high ethylene/ethane adsorption selectivity. Nevertheless, most of these existing adsorbents displayed preferential adsorption of ethylene over ethane by π -complexation bonds. Thus, the adsorption separation based on these adsorbents would not yet economically feasible. The reasons are as follows: (1) since the π -complexation bond is a type of weak chemical bond, thus the desorption of ethylene from the π -complexation adsorbents will consume more energy than the physisorption ones; and (2) the cracked gas mixture as a feed contains large amounts of ethylene, for instance, the ethylene/ethane ratio in the cracked gas mixture is about 15:1, and thus if the π -complexation adsorbents was applied to separate ethylene from ethane by means of PSA or VSA, its productivity of ethylene at 99.8% purity would be low (Liao et al., 2015). The preferential adsorption of ethylene implies an additional desorption stage, generally by applying vacuum or using an inert gas, and at least four adsorption–desorption circles are necessary to achieve the high purity required by the ethylene polymerization reactor, resulting in consumption of the extra energy (Da Silva and Rodrigues, 2001; Vogler and Sigrüst, 2006). In the other words, if ethane could be preferentially adsorbed through the physisorption, the purified ethylene will be directly obtained during the adsorption step, which would simplify the whole separation scheme and reduce the energy consumption, especially for the separation of cracked gas. van den Bergh et al. (2011) and Gucuyener et al. (2010) studied the ethane/ethylene adsorption performance of zeolite imidazolate framework ZIF-7, and found that ZIF-7 was an ethane-selective adsorbent through the gate-opening mechanism, and its ethane uptake of ZIF-7 was about 2 mmol/g at 298 K and 100 kPa. And then Chen et al. (2015) employed the breakthrough experiments to determine the ethane/ethylene adsorption selectivity of ZIF-7, and reported that its ethane selectivity was about 2 at $25\text{ }^\circ\text{C}$ and 120 kPa. Pires et al. (2014) and Pillai et al. (2015) reported that IRMOF-8 exhibited the characteristic of adsorbing ethane preferentially, with the ethane uptakes about 4.0 mmol/g at 298 K and 100 kPa, and meanwhile, its ethane/ethylene adsorption selectivity was below 2. Recently, Liang et al. (2016) synthesized a metal-organic framework material Ni(bdc)(ted)_{0.5} with double ligands (bdc and ted) and reported that its C_2H_6 adsorption capacity was up to

6.93 mmol/g at 100 kPa and 273 K, and its C_2H_6/C_2H_4 adsorption selectivity was in the range of 2–7.8 at pressure below 100 kPa, higher than the reported adsorbents possessing the characteristic of preferential adsorption of C_2H_6 over C_2H_4 . Nevertheless, if these MOFs are put into industrial applications, it is still faced with the challenge of cost, stability and scaling up of MOFs (Li et al., 2009; Tan et al., 2012).

Recently, some new activated carbon materials with high specific surface area and gas adsorption capacity have been reported (To et al., 2016; Sethia and Sayari, 2015; Ludwinowicz and Jaroniec, 2015). For example, Xian et al. (2016) prepared a series of novel carbonized polydopamine adsorbents (C-PDAs) using dopamine as carbon source, and reported that the BET surface area and pore volume of C-PDAs were separately up to 3342 m^2/g and 2.01 cm^3/g . More interestingly, CO_2 adsorption capacity of C-PDAs reached up to 30.5 mmol/g at 25 bar, and 5.8 mmol/g at 1 bar, much higher than most of MOFs. It was mainly ascribed to its high surface area and the surface basic site concentrations. Wang et al. (2016) examined the adsorption properties of C-PDAs for C_2H_6/C_2H_4 , and it was found that C-PDAs showed significantly preferential adsorption of C_2H_6 over C_2H_4 . Its C_2H_6 adsorption capacity was up to 7.93 mmol/g at 100 kPa and 298 K, and its C_2H_6/C_2H_4 adsorption selectivity was in the range of 1.9–7.94 at pressure below 100 kPa. Jajilov et al. (2015, 2016) used asphalt as carbon source, and prepared new ultra-high surface area porous carbons by two-step synthesis method (carbonization and activation steps) for CO_2 adsorption. These materials exhibited high CO_2 adsorption capacities at high pressure. For example, their CO_2 adsorption capacities were up to 21 mmol/g at 30 bar and $25\text{ }^\circ\text{C}$, and 35 mmol/g at 54 bar and room temperature. Since asphalt is the readily available and inexpensive mixture of hydrocarbon produced from petroleum distillation residue and it mainly consists of naphthene aromatics and polar aromatics, it was worthy of utilizing the asphalt as carbon source for preparing new porous carbon materials for C_2H_6/C_2H_4 adsorption separation. However, to the best of our knowledge, none of studies about the asphalt-based porous carbon materials for the adsorption separation of C_2H_6/C_2H_4 has been reported yet.

The purpose of this work is to investigate novel asphalt-based activated carbons (A-ACs) for C_2H_6/C_2H_4 adsorption. Asphalt (a very inexpensive carbon source and a readily available byproduct of petroleum refinery using crude oil) was used as carbon source to prepare a series of asphalt-based activated carbons (A-ACs) using one-step synthesis method, and then the resultant A-ACs were characterized by N_2 adsorption. Scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). C_2H_6 and C_2H_4 isotherms on A-ACs were measured separately at different temperatures. C_2H_6/C_2H_4 adsorption selectivity of A-ACs was calculated by means of Ideal adsorbed solution theory (IAST). And the isosteric heats of C_2H_6 and C_2H_4 adsorption on A-ACs were estimated by the Clausius-Clapeyron equation. The binding energies (BE) between ethane/ethylene and substrate and the preferential adsorption mechanism of C_2H_6 over C_2H_4 on A-ACs were discussed. And the influence of heteroatom O and N on the ethane adsorption of A-ACs was discussed and reported here.

2. Experimental

2.1. Materials

Asphalt (GB/T 494-2010) was provided by Panther Building Materials Co. Ltd. Potassium hydroxide (KOH) and hydrochloric acid (HCl) were purchased from Guangzhou Guanghua Sci-Tech Co. Ltd. Carbon tetrachloride (CCl_4 , 99.5%) was obtained from Tianjin Damao Chemical Reagent Factory. For the adsorption tests, the

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