



A novel fructose-based adsorbent with high capacity and its ethane-selective adsorption property



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ABSTRACT

Separation of ethane/ethylene mixture at normal temperature and pressure is a challenging issue in the petrochemical industry. Herein, we synthesized Fructose-based carbon materials (C-Frus) with characteristic of ethane-selective adsorption for the energy-effective separation of ethane and ethylene. The as-synthesized sample C-Fru-4-700 exhibited narrow micropore size distribution and high micropore volume. More importantly, these samples presented preferential adsorption of C₂H₆ over C₂H₄, of which the ethane capacity of the sample C-Fru-4-700 reached as high as 7.94 mmol/g at 25 °C and 100kPa, much higher than that of many MOFs, and its selectivity for equimolar C₂H₆/C₂H₄ mixture reached 4 at low pressure. These excellent properties made C₂H₆/C₂H₄ mixture be well separated by fixed bed at 25 °C. Computational simulations revealed that the surface O_{site1}, O_{site2} and O_{site3} sites of the materials are the favorably adsorptive sites of C₂H₆. Fructose-based carbon materials are promising for separation of ethane/ethylene mixture at normal condition.

1. Introduction

As the monomers in plastic industrial and paramount intermediates for synthesizing various chemicals, the demand for C₂H₄ and C₂H₆ is huge [1]. Separating C₂H₄/C₂H₆ is challenging due to their similar molecule diameters and low relative volatilities. Cryogenic high-pressure distillation, as the current separation process to obtain high purity olefin, consumes massive fossil energies and becomes one of the most energy-intensive processes for chemical industry [2,3]. Extensive efforts have been paid to deploy alternatives for the olefin purification and adsorption separation process is one of the most promising approach due to its simple infrastructure and non-thermal operation [4–6].

An adsorbent with high capacity and selectivity is the key factor in adsorption technology. Numerous adsorbents reported for C₂H₆/C₂H₄ separation can be distinguished to two categories, ethylene-trapping and ethane-trapping adsorbents [4], including metal organic frameworks [4,7,8], carbons [9–11] and zeolites [12,13]. Typical ethylene-trapping adsorbents with high selectivity are based on π -complexation [14], such as (Cr)-MIL-101-SO₃H with Ag(I) modification [15], PAF-1-SO₃Ag [16], Cu(I)-decorated MIL-100(Fe) [17], MIL-100(Fe) [18]. However, since the π -complexation is weak chemisorption, more energies are required for desorbing ethylene from the adsorbents.

Furthermore, the use of ethylene-trapping adsorbents would make it very difficult to produce polymerization grade ethylene with purity of 99.95% by using a simple adsorption–desorption cycle [11]. If the ethylene-trapping adsorbents were used, at least four adsorptions–desorption cycles and five-step fashion would be required [2,19], which would make the separation of ethylene and ethane become complex and energy-consuming. The ethylene-trapping adsorbents are not considered as ideal adsorbents. This problem can readily be solved by developing ethane-trapping adsorbents. The polymerization grade ethylene can be obtained with the help of a simple adsorption–desorption process at normal temperature. Therefore, developing ethane-selective adsorbents is vital and significant.

For now, some MOFs have been reported to preferentially adsorb ethane. For example, ZIF-7 [19], an ethane-selective adsorbent, can separate C₂H₄/C₂H₆ mixture via a special mechanism of gate-opening. Böhme et al. reported that ethane capacity of ZIF-8 was higher than ethylene, implying preferential adsorption of ethane and the ethane absorbed amounts reached 2.5 mmol/g at 100 kPa [20]. Suvendu et al. reported ZIF-318 can extract ethane from olefin/paraffin mixture with the uptake of 1.25 mmol/g [21]. Liao et al. designed and synthesized MAF-49 and its capacity for C₂H₆ and C₂H₄ were 1.42 and 0.85 mmol/g respectively [2]. Recently, Chen et al. reported two kinds of iron-based MOFs PCN-250 [22] and MIL-142A [23] with preferential adsorption of

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ethane. In addition, some MOF also exhibited good adsorption capacity for C_2H_6 at 25 °C and 100 kPa, such as $[Ni(bt- zip)(H_2btzip)] \cdot 2DMF \cdot 2H_2O$ (88.9 cm^3/g) [24], $\{[Sr(BDPO)_{0.5}(H_2O)]_2H_2O\}_n$ (1) (51.3 cm^3/g) [25], $\{[Ba_2(BDPO)(H_2O)] \cdot DMA\}_n$ (71.5 cm^3/cm^3) [26]. However, MOFs still face challenges of enhancing water vapor stability, lowering cost, and improving adsorption capacity and selectivity before being applied in industrial application.

It is noticed that some novel carbon materials were recently developed by using new carbon sources for C_2H_4/C_2H_6 separation due to excellent stability and outstanding capacity. Xian et al. [27] successfully synthesized C-PDAs derived from dopamine and then Wang et al. [10] examined their C_2H_6/C_2H_4 adsorption properties. It was reported that C-PDAs can selectively adsorb ethane with super-high capacity of 7.93 mmol/g at normal condition. Liang et al. prepared asphalt-based A-ACs [28] derived from asphalt and its composite C-PDA@A-ACs [11], and both porous adsorbents belonging to ethane-selective adsorbents exhibited superior ethane uptake which was above 7 mmol/g. Breakthrough experiments proved that olefin and paraffin can be separated by using a simple adsorption process with these adsorbents. The results above indicated that adsorption separation performances of these carbon materials derived from new carbon sources were comparable to or superior to many MOFs, and it also implied that the use of new carbon sources to synthesize porous carbon materials would be mostly possible to obtain novel adsorbents with excellent performance for C_2H_4/C_2H_6 separation.

Herein, we reported novel ethane-selective biomass carbon materials C-Frus derived from fructose with superior capacity and ethane-selective adsorption property. The texture property was determined by nitrogen adsorption at 77 K. The morphology was characterized by Scanning electron microscopy (SEM). Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were also applied to analyze its surface chemical property. C_2H_6 and C_2H_4 isotherms as well as isosteric heats were measured. The static and dynamic separation performance were evaluated by ideal adsorbed solution theory calculation and breakthrough experiments separately. Mechanism of preferential affinity with ethane on fructose-based material C-Frus would be investigated and reported here.

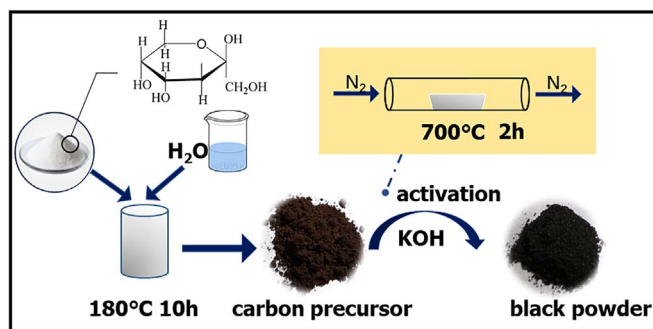
2. Experimental section

2.1. Chemicals and reagents

All reagents were commercially available and used as received without further purification. Fructose was obtained from Shanghai Boao Food Sci-Tech Co. Ltd. Potassium hydroxide (KOH) and hydrochloric acid (HCl) were purchased from Guangzhou Guanghua Sci-Tech Co. Ltd. For the adsorption tests and the breakthrough experiments, the gases used were C_2H_6 (99.99%, Guangzhou ShengYing), C_2H_4 (99.99%, Guangzhou ShengYing).

2.2. Preparation of samples C-Frus

Hydrothermal carbonization (HTC) [29] was applied to prepare the carbon precursor derived from fructose. The preparation process is illustrated in Scheme 1. In detail, procedure of preparation was as follows: 4 g of fructose was added to 40 mL DI water and kept stirring until the solute was dissolved completely. Then, the solution was transferred into a Teflon autoclave reactor. To obtain carbon precursor, Teflon autoclave reactor was heated and maintained at 180 °C for 10 h for polymerization and carbonization reactions [30]. During the reaction, some aromatic compounds and oligosaccharides were formed, which was known as polymerization, followed by carbonization step [30]. After the reaction, the black products in the yellow solvent were collected by filtration, followed by being washed thoroughly with distilled water and ethanol until the filtrate was clear, and then dried at 100 °C for more than 6 h to remove the remaining solvent in the



Scheme 1. The preparation process of C-Fru-X-700.

materials. The carbon precursors were grinded well with KOH at four different C/KOH weight ratios (1:2, 1:3, 1:4). The homogeneous mixture was transferred to a quartz boat, then the quartz boat was placed in a horizontal tube furnace, followed by being heated at a heating rate of 5 °C/min with N_2 flow at 60 mL/min, and the horizontal tube furnace was maintained at specific temperature (675 °C, 700 °C, or 725 °C) for 2 h. After that, the activated carbon materials were first soaked in 1 M HCl with steadily stirring for 4 h to remove the remnant KOH and some resulting potassium oxide, and then the materials were further washed by distilled water thoroughly until the filtrate was neutral. Finally, the materials were dried in an oven at 100 °C for 6 h. The resulting samples were identified by C-Fru-X-Y, where X represents the weight ratio of KOH/C, Y represents the activation temperature. For example, C-Fru-2–700 represents that the activated carbon was prepared at 700 °C and the KOH/C ratio of 2.

2.3. Characterizations

The texture property of the samples was characterized with Micrometrics ASAP 2460 by N_2 adsorption/desorption experiment at 77 K. The Brunauer-Emmett-Teller (BET) surface area was calculated at P/P_0 in the range of 0.05–0.2, pore distribution was calculated by DFT method using desorption branched of isotherm, and the pore volume was evaluated by t-plot method. The morphologies were observed on Hitachi S-4800 scanning electron microscope after depositing a thin layer of gold on the sample. Raman spectroscopy was conducted on a Horiba Jobin-Yvon ARAMIS Raman apparatus. The analysis of relative content of oxygen and carbon was conducted on Thermo-VG Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). Prior to each measurement, all C-Frus samples were degassed under vacuum at 150 °C for 6 h.

2.4. Measurement of C_2H_6 and C_2H_4 adsorption isotherms

C_2H_6 and C_2H_4 adsorption isotherms were measured with the Micrometrics 3Flex surface characterization analyzer separately at 15 °C, 25 °C and 35 °C. Prior to each measurement, the sample (~70 mg) was outgassed at 150 °C under vacuum ($< 10^{-5}$ kPa) for 6 h.

3. Results and discussion

3.1. Characterization of C-Frus

As shown in Fig. 1, all the nitrogen adsorption-desorption isotherms (77 K) were identified as typical type-I profiles, indicating extraordinary micro porosity of the C-Frus samples. Additionally, there were no hysteresis loops being observed, manifesting that there were less mesopores in the materials. Fig. 2 gives information about the pore size distributions (PSD). It is clearly visible that all the pore sizes mainly fell into the micropore region (< 2 nm) although the distribution was somewhat wider. Fig. S1 and Fig.S2 show the N_2 adsorption

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