Cyclodextrin Covalent Organic Framework for Light Hydrocarbons of C$_4$ Separation

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Abstract. Light hydrocarbons of C$_4$ are very important raw materials in chemical production. However, due to the close physical properties between C$_4$ light hydrocarbons, it is difficult to completely separate them. The covalent organic framework (COF) used for adsorption and separation of C$_4$ is an alternative to traditional separation methods. The designable structure and developed pores of COF have enormous potential for application in the field of separation. Herein, γ-CD-COF (CD=cyclodextrin) has been synthesized for the separation of n-C$_4$H$_8$/1,3-C$_4$H$_6$. Single-component adsorption data indicates that it has a difference in the maximum adsorption capacity for n-C$_4$H$_8$ (35.5 cm^3 g^{-1}) and 1,3-C$_4$H$_6$(58.8 cm^3 g^{-1}). The dynamic breakthrough experiments proved that γ-CD-COF has great potential for the separation of n-C$_4$H$_8$/1,3-C$_4$H$_6$.

Keywords: light hydrocarbons; n-C4H8; 1,3-C4H6; separation; γ-CD-COF.

1 Introduction

Gas light hydrocarbons of C1 to C4 are not only important fuels (such as gasoline, diesel, and kerosene), but also important raw materials for the production of many chemicals and materials. They plays an important role in the global energy structure and the chemical and petrochemical industries. In industrial production, gaseous light hydrocarbons of C1 to C4 typically exist in the form of mixtures. Due to the close physical properties between gas mixtures, such as molecular size, relative volatility, boiling point. Low-temperature distillation is commonly used in industry for separation, which often involves significant energy consumption.

Light hydrocarbons of C4 include olefins such as 1,3-C4H6, n-C4H8 and i-C4H8, as well as alkanes such as n-butane and isobutane [1, 2]. N- C4H8 can be used to produce alkyl gasoline, detergent alcohols, synthetic lubricants, plasticizers and so on; Isobutene is a raw material for the synthesis of methacrylonitrile, polyisobutene, antioxidants, tert butyl ether and synthetic elastomers. In industrial production, C4 is mainly produced through fluid-catalytic-cracking (FCC), forming C4H6, n-C4H8, i-C4H8, and a small amount of butane mixture [3]. However, due to the close physical properties

such as molecular size, boiling point, and dipole moment between C4, it is difficult to completely separate them [4, 5].

The adsorption separation method is a potential energy-saving separation technology [6-8], avoiding the problem of high energy consumption. The adsorption separation method has a wide range of applications in wastewater adsorption, mainly manifested in the process of using the physical and chemical adsorption properties of solid adsorbents to remove various pollutants from wastewater. In the application of gas adsorption separation, the method of adsorption could also be divided into three types: physical adsorption, chemical adsorption, and ion exchange adsorption. Activated carbon (AC) has a good effect in the separation of light hydrocarbons. In the adsorption process of activated carbon, the intermolecular attraction is mainly van der Waals force. When molecules came into contact with the pore surface of activated carbon, the van der Waals forces between molecules will bind the molecules to the pore surface of activated carbon, forming surface adsorption. Deep adsorption is due to the formation of chemical bonds between molecules and atoms inside the pores of activated carbon, allowing molecules to be firmly adsorbed inside the pores of activated carbon. It should be noted that the adsorption capacity of AC is limited. When AC reached saturation, it could not adsorb more molecules. Therefore, in order to develop new materials for gas adsorption is important.

Covalent organic frameworks (COFs), as a new type of crystalline porous material, have wide applications in the field of gas separation [9]. It is possible to design COFs with different functions and appropriate pore sizes to realize the adsorption and separation of gas molecules, improving the separation efficiency.

Cyclodextrin molecules are easy to crystallize, and the abundant hydroxyl groups in their structure can serve as nucleophilic sites, providing opportunities for connecting cyclodextrin to construct extended structures. At the same time, cyclodextrin has a special hydrophobic cavity structure and the cavity could have interactions with guest molecules, which called host-guest interactions. Introducing it as a building block into the COF field could further enrich the kind of structure and function of COFs. In this article, the ester exchange reaction between trimethyl borate and hydroxyl groups was used for the polymerization process. By carefully optimizing the proportion of monomers, the amount of counter ions, the type and proportion of mixed solvents, and the temperature and time of the reaction, the synthesis of COF with uniform size and good quality was successfully achieved. The successful occurrence of the crosslinking process was demonstrated by infrared spectroscopy, solid-state nuclear magnetic resonance, and changes in gas adsorption capacity and thermal stability before and after crosslinking.

Herein, the γ-CD-COF powders were successfully prepared with a high Brunauer-Emmett-Teller (BET) surface area and the pore size is mainly about 0.6 nm which is slightly larger than that of butane [10]. Considering the microporous and developed specific surface area of COF, single-component gas adsorption tests of C_4 were performed to evaluate the separation potential. Comparing the adsorption rate and equilibrium amount, the separation of $1,3$-C_4H_6/n-C_4H_{10} was selected. It has been proven through the dynamic column breakthrough experiments that γ-CD-COF has potential in separate $1,3$-C_4H_6/n-C_4H_{10}.

2   Methodology

γ-CD-COF powder was synthesized following the previously reported procedure [10]. γ-CD (0.1300 g, 0.100 mmol), LiOH (0.0132 g, 0.551 mmol), B(OMe)$_3$ (59.5 µL, 0.524 mmol), super dry DMF (8 mL) and super dry mesitylene (7 mL) into a 30 mL microwave glass vial were added in a glove box. The reaction was reacted at 120°C with stirring under microwave conditions for 4 h. The white powder was collected through centrifugation, and purified through repeated washing with DMF and acetone. Finally, the solid was dried under 80 °C for 2 h to give γ-CD-COF with a yield of 80%.

3   Results

The chemical structure of γ-CD-COF through the performance of FT-IR. (Figure 1 A) and the change of solubility. There is a significant difference in solubility between the obtained γ-CD-COF and γ-CD. γ-CD can dissolve rapidly in DMF solvent, while γ-CD-COF can exist stably in DMF solvent. The difference in solubility can preliminarily indicate successful crosslinking. The characteristic peak at 1417 cm-1 represents the stretching vibration of B-O, and the peak at 665 cm-1 is the bending vibration of the newly formed C-H bond. In addition, we also performed power X-ray diffraction (PXRD) patterns to evaluate the crystallinity of γ-CD-COF powder (Figure 1 B), the PXRD matches well with the simulated PXRD pattern obtained from the reported structure, demonstrating the successfully crosslinked.
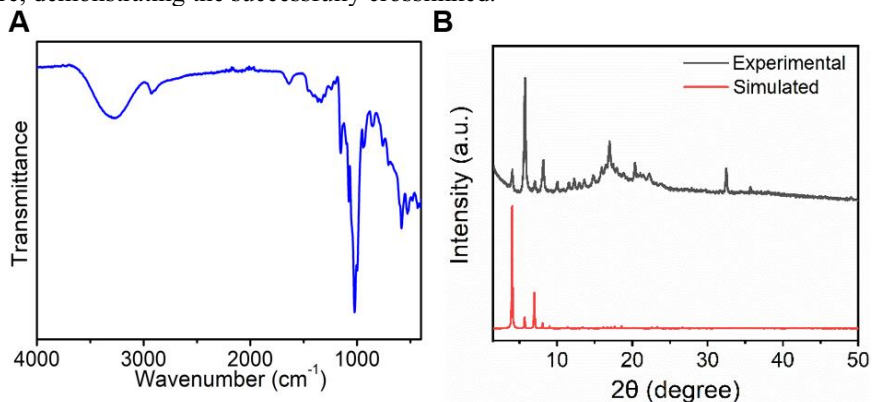

Fig. 1. The FT-IR spectroscopy of γ-CD-COF (A) and the PXRD patterns of γ-CD-COF (B).

Argon sorption isotherm was performed at 87 K to explore the porosity of γ CD-COF. As shown in Figure 2, γ-CD-COF shows a type-I adsorption-desorption isotherm characteristic with a steep increase in capacity at relatively low pressures, indicating the microporous characteristic of the sample. The specific surface area of γ-CD-COF calculated by the BET model is around 630 m2 g-1. The pore size distribution is mainly about 0.6 nm calculated according to the nonlocal density functional theory (NLDFT), indicating that the microporous and developed pores of COF can be used for the

adsorption and separation of C4. In addition, the above results indicate that the stability of the framework of γ-CD is greatly improved after covalent bonding with B(OMe)$_3$, and the pore structure can still be maintained after removing solvent molecules.
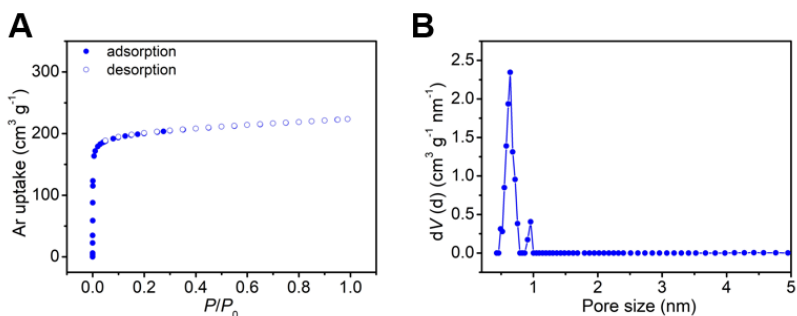

Fig. 2. Ar adsorption/desorption isotherms at 87 K (A) and pore size distributions (B) of γ-CD-COF.

To evaluate the separation potential of C4, single-component gas adsorption tests were performed on n-C4H10, 1-C4H8, i-C4H8, and 1,3-C4H6. The maximum adsorption capacities of CD-COF powder for n-C4H10, 1-C4H8, i-C4H8, and 1,3-C4H6 are 35.5 cm3 g-1, 53.7 cm3 g-1, 46.9 cm3 g-1, and 58.8 cm3 g-1(Figure 3), respectively. The difference in equilibrium adsorption capacity between n-C4H10 and 1,3-C4H6 is the largest. Moreover, the separation potential of n-C4H10 and 1,3-C4H6 was evaluated by the Ideal Adsorption Solution Theory (IAST), and the mathematical formula is as follows. According to the formula, the IAST selectivity of n-C4H10/1,3-C4H6 was 1.65, indicating that it has separation potential for n-C4H10/1,3-C4H6 by using γ-CD-COF. Therefore, we chose the n-C4H10/1,3-C4H6 system for separation testing.
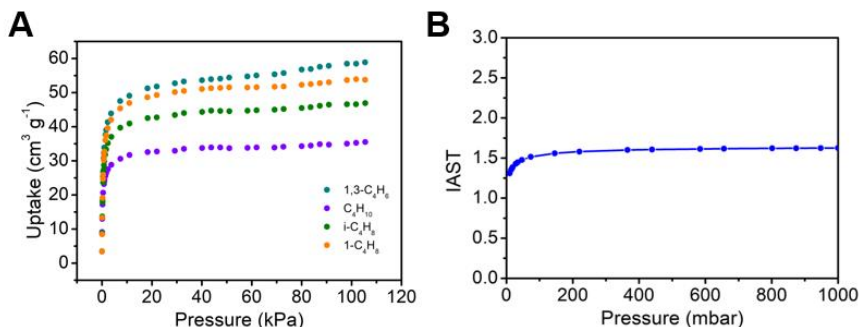
$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad (1)$$

Fig. 3. Single-component adsorption test curve of γ-CD-COF to C$_4$ (A) and the IAST selectivity of n-C$_4$H$_{10}$/1,3-C$_4$H$_6$ (B).
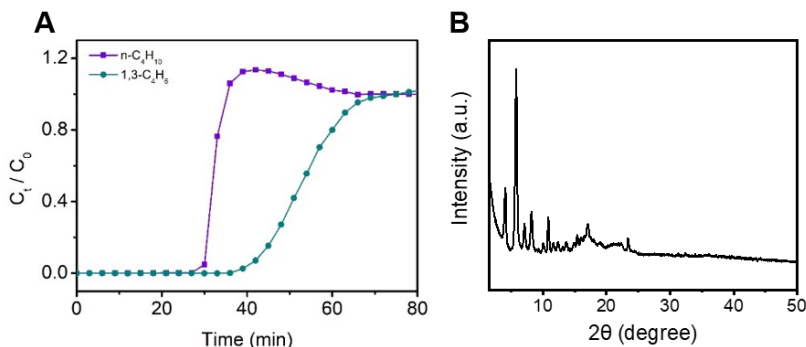
Fig. 4. Dynamic column breakthrough tests for γ-CD-COF with the gas mixture of n-C₄H₁₀/1,3-C₄H₆ (14:1, v/v) at 298 and 1 bar (A). The PXRD patterns of γ-CD-COF after Dynamic column breakthrough tests (B).

Dynamic column breakthrough tests were performed to further evaluate the purifying ability of γ-CD COF powder to separate n-C4H10 and 1,3-C4H6 mixtures, which was carried out by laboratory-built breakthrough device. The breakthrough experiments were performed in a packed column of activated γ-CD-COF powder under flow (0.75 mL min-1) of binary n-C4H10/1,3-C4H6 (14:1, v/v) mixtures at 298 K to simulate the actual application process of FCC. From the breakthrough curve (Figure 4 A), it can be seen that n-C4H10 first passed through the mixture of n-C4H10/1,3-C4H6 at 30 min and was detected by chromatography, while the 1,3-C4H6 was detected after 10 mins. High purity n-C4H10 can be collected during this period. Moreover, the PXRD (Figure 4 B) showed the crystallinity of γ-CD-COF was still well maintained after the breakthrough tests. Comparing with the γ-CD-COF synthesized at first, there was no significant change in crystallinity. The results showed that γ-CD-COF is stable in separate n-C4H10/1,3-C4H6 and has high separation ability, which is probably attributed to different affinity to n-C4H10 and 1,3-C4H6, indicating that it is promising for efficient separation of C4 gas in practical production.

4   Conclusions

In conclusion, we synthesized γ-CD-COF with a high specific surface area. Considering the different affinity of γ-CD-COF towards n-C₄H₁₀ and 1,3-C₄H₆, n-C₄H₁₀ can be first detected by chromatography in the mixture of n-C₄H₁₀/1,3-C₄H₆, while 1,3-C₄H₆ is adsorbed in the pores of γ-CD-COF, which can satisfy the separation of the n-C₄H₁₀/1,3-C₄H₆. In addition, DFT theoretical calculations should be conducted to further demonstrate the adsorption capacity of the framework for C4 molecules, we also need to compare with commercial adsorbents, such as AC, ZIF-8 and molecular sieve. they are what we need to continue exploring next step. This work provides an efficient and economical separation method for chemical production. On this basis, we can improve the adsorption and separation capabilities by optimizing the pore size and shape of pores of COF. We could change the type of cyclodextrin to obtain different cyclodextrin-based

COFs, such as α-CD-COF, β-CD-COF. What is more, We can also obtain single crystals of cyclodextrin-based COFs by adjusting the dose of solvent or the kind of solvent, the regular spatial structure and appropriate pore size are more conducive to mass transfer and separation of gas molecules. It maybe have unexpected results. We believe that this strategy will make significant contributions to enrich the variety, functionality, and application scope of COFs in the future.

Acknowledgments

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