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Characteristics of carbon dioxide adsorption on β-cyclodextrin/cellulose composite material

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Abstract: The work focused on the preparation and characterization of porous composite material as novel adsorbent towards CO_2. The porous composite material was synthesized by cross-linking of cellulose and β-cyclodextrin with epichlorohydrin (EPI). Then the adsorption characteristics of carbon dioxide on the porous composite material, such as adsorption capacity and selectivity were experimentally investigated. The experimental results showed pulp cellulose in selected types of cellulose was more suitable for the synthesis of CO_2 composite adsorbent. Meanwhile, the analysis from BET and FTIR indicated that the β-cyclodextrin was grafted pulp cellulose by epichlorohydrin. The grafted cellulose led to the surface area and pore size of β-cyclodextrin increased by 3.78 and 2.96 times. Compared with CO_2 adsorption capacity of 3.186cm^3/g on the β-cyclodextrin, EPI/PC-CD composite exhibited a higher capacity of CO_2 adsorption(8.613cm^3/g) at 298K and 1bar, accompanying an endothermic process and the isosteric heat between 72 and 78kJ/mol. Moreover, the adsorption selectivity of CO_2 over N_2 retained above 13 at 298K.

Introduction

Global warming resulted from the emission of greenhouse gases has received much attention recently. Various CO_2 capture technologies, such as chemical absorption, adsorption and membrane, have been exploited to reduce CO_2 emissions [1]. However, the conventional absorption processes such as alkanolamine aqueous solutions still possess some drawbacks, e.g, high equipment corrosion rate, high energy consumption in regeneration; whereas the membrane technologies have not yet been matured for disposing huge amount of flue gas due to the existence of significant mass transfer limitations. As a result, adsorption processes are well received as the effective approaches to overcome these inherent problems by using some high-efficient adsorbents, such as activated carbon[2-4], 13X molecular sieve [5,6] and various other silicate materials[7,8].

The investigations of CO_2 encapsulation and complexation with cyclodextrins have indicated that β-cyclodextrin could form cyclodextrin based nanosponges with inclusion of CO_2. However, the literatures related to CO_2 capture of composite from β-cyclodextrin through cross-linking[9] for gaseous phase catalytic synthesis and the reduction of CO_2 emission are very limited. Moreover, those derivatives were restricted in their application. Thereby, it is necessary to synthesize eco-friendly CO_2 adsorbent based on β-cyclodextrin with less use of those poisonous chemicals.

Recently, cellulose has drawn increasing attention as reinforcing agents in polymer composites[10,11] due to biodegradable, easy obtaining and little investing. Although the literature related to CO_2 inclusion by cellulose for gaseous phase catalytic synthesis and the reduction of CO_2 emission [12,13] have been limited reported, the application of porous composite material of cellulose/β-cyclodextrin for CO_2 uptake still remains available for exploration. In order to prepare the porous composite material as CO_2 adsorbent, epichlorohydrin (EPI) was used as a coupling agent to achieve the cross-linking of cellulose and β-cyclodextrin. Meanwhile, the porous composite material was characterized by Brunauer-Emmett-Teller(BET) theory, Fourier Transform

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Infrared (FTIR) spectra, Then its performances of gas adsorption, such as adsorption capacity of CO_2 and selectivity of CO_2 over N_2 were experimentally investigated.

Materials and methods

Materials

Pulp cellulose was obtained from Money Printing Plant in Baoding. Microcrystalline cellulose (MCC, 99% purity), β-cyclodextrin (β-CD) powder (98% purity) and epichlorohydrin (EPI) were purchased from Shanghai Aladdin Biochemical Polytron Technologies Inc. Ethanol(anhydrous), sodium hydroxide and urea came from Tianjin XingFu Technology Development Co., Ltd. All these chemicals were used as received without further purification.

2.2. Synthesis and characteristics of porous adsorbent

The porous adsorbents were prepared by the cross-linking of cellulose and β-cyclodextrin (β-CD) with EPI. Firstly, the cellulose was dissolved in a flask (100ml) with the solution (48ml) of sodium hydroxide(3.5%w/w) and urea(6%w/w) followed by the addition of β-cyclodextrin (β-CD) and stirring until the system was well mixed. Then some amount of EPI was gradually and slowly added to this system in 20min. The solution was kept at certain temperature for 4hrs, then precipitated with 50ml of ethanol. The precipitate was treated by washing with distilled water/ethanol, product was obtained through filtering and drying under vacuum overnight.

The adsorption isotherms of CO_2 at 298K and 273K was experimentally obtained based on volumetric gas adsorption method. The as-prepared porous material, PC and β-CD were recorded by using Tensor II FTIR spectroscopy (BRUKER Technologies) associated with diffuse reflectance accessory (PURGE Technologies). The BET surface areas of as-prepared porous Material and β-CD were analyzed based on volumetric gas adsorption method(P/P_0=0.05~0.35) with the measurement using JW-BK122W static nitrogen adsorption analyzer(JWGB Sci& Tech Co. Ltd , Beijing) at 77K.Then their pore size distributions were obtained based on BJH and HK methods.

Results and discussion

Influence of cellulose type on CO_2 adsorption

In our synthesis, Epichlorohydrin was used to prepare the porous adsorbents through the cross-lingking of β-cyclodextrin with various cellulose, which were respectively referred as EPI/PC-CD for pulp cellulose, EPI/MCC-CD for microcrystalline cellulose. Then CO_2 adsorption characteristics of these composite adsorbents at 298K are presented in Figure 1. As presented in Figure 1, the capacities of CO_2 adsorption on these composite adsorbents increased with increasing gas pressure of CO_2, which were 3.342cm^3/g for EPI/MCC-CD, 8.613cm^3/g for EPI/PC-CD when the gas pressure was 1bar. The composite adsorbent EPI/PC-CD exhibited higher capacity of CO_2 adsorption, indicating that cellulose type had a significant effect on CO_2 adsorption performance and pulp cellulose was suitable for β-cyclodextrin to prepare the porous material as CO_2 adsorbent.

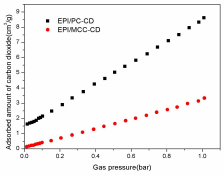


Figure.1 CO_2 adsorption on as-prepared adsorbents from different cellulose

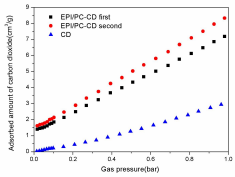


Figure. 2 Capacity change of CO_2 adsorption based on parallel tests

Influence of cross-linking parameters on CO_2 adsorption

In consideration of obviously higher capacity of CO_2 adsorption on EPI/PC-CD than EPI/MCC-C D, the effects of cross-linking parameters such as cross-linking temperature, mass ratio of β-CD to PC and EPI dosage, on CO_2 adsorption of EPI/PC-CD were experimentally investigated based on orthogonal method and the results are listed in Table 1. As seen from Table 1, the capacity of CO_2 adsorption on the porous composite adsorbent EPI/PC-CD varied in the range of 2.054 to 8.613cm^3/g. The EPI dosage exhibited the most significant effect on CO_2 adsorption of EPI/PC-CD,

followed by mass ratio of β-CD to PC and cross-linking temperature. This indicated that EPI dosage was the key parameter in the synthesis of EPI/PC-CD and the CO_2 adsorption performance of EPI/PC-CD could be improved by modifying these cross-linking parameters. The optimum conditions(denoted as β-CD/PC-1-4-333) determined by analysis of orthogonal method included that the synthesis temperature was 333K, mass ratio of β-CD to PC was 1:1 and the EPI Dosage was 4ml/(1g β-CD).

Two parallel samples based on above optimum conditions was tested, and the results of CO_2 adsorption are shown in Figure 2. As seen from Figure 2, the capacity of CO_2 adsorption at 1bar and 298K varied in the range of 7.427 to 8.613cm^3/g. Compared with CO_2 adsorption capacity of 3.186cm^3/g on pure β-CD without the cross-linking of PC, the porous composite adsorbent EPI/PC-CD with the cross-linking of PC exhibited a higher capacity of CO_2 adsorption(7.427-8.613cm^3/g) at 1bar and 298K.

Table 1 Analysis of orthogonal method for CO_2 adsorption

sample	β-CD/PC mass ratio	EPI dosage(ml)	Cross-linking temperature(K)	CO_2 uptake(cm^3/g)
β-CD/PC-1-2-313	1	2	313	4.573
β-CD/PC-1-4-333	1	4	333	8.613
β-CD/PC-1-6-353	1	6	353	2.550
β-CD/PC-0.5-2-333	0.5	2	333	3.196
β-CD/PC-0.5-4-353	0.5	4	353	3.054
β-CD/PC-0.5-6-313	0.5	6	313	3.655
β-CD/PC-2-2-353	2	2	353	2.587
β-CD/PC-2-4-313	2	4	313	3.914
β-CD/PC-2-6-333	2	6	333	2.054
k1	5.245	3.452	4.047	
k2	3.302	5.194	4.621	
k3	2.852	2.753	2.730	
Delta	2.394	2.441	1.891	
	2	1	3	

Adsorbent characteristics

The tests of BET of β-cyclodextrin aggregates and solid acid derivative were conducted to study surface area and pore structures. β-CD exhibited only 5.34 m^2/g of specific surface area and 1.03×10^{-2} cm^3/g of pore volume with a mean pore size of 34 nm. In contrast, the EPI/PC-CD obtained after the cross-linking PC by EPI exhibited 20.22 m^2/g of specific surface area and 3.05×10^{-2} cm^3/g of pore volume, which were 3.78 and 2.96 times higher than native β-cyclodextrin aggregates. Meanwhile, the mean pore size of EPI/PC-CD decreased into 30nm. The higher specific surface area and pore volume with decreased mean pore size of EPI/PC-CD, compared with β-cyclodextrin aggregates, indicated that the crosslinking PC by EPI led to the formation of porous structure of the composite.

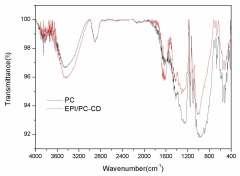


Figure 3. FTIR spectra of pulp cellulose and EPI/PC-CD composite

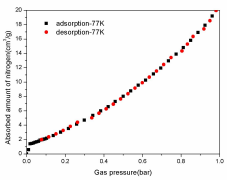


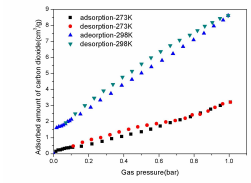
Figure 4. Isotherms of N_2 adsorption and desorption at 77K

Meanwhile, those functional groups on the surface of solid acid derivative were demonstrated by the results FTIR spectra of pulp cellulose and EPI/PC-CD composite presented in Figure 3. As seen in Figure 3, the peak type and wave number of the infrared spectra of PC and EPI/PC-CD composite are similar because β-cyclodextrin aggregates and pulp cellulose owned similar groups. Compared pulp cellulose, the intensities of the peaks between 3450 and 3500 cm^{-1} due to O-H

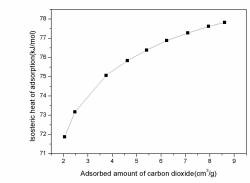
stretching vibration and between 1600 and 1700 cm^{-1} due to the O-H bending vibration were also obviously increased. In addition, the intensities of peaks between 2850 and 2900 cm^{-1} due to C-H stretching vibration unchanged, Finally, the intensities of peaks at 1300 cm^{-1} due to C-O stretching vibration was shifted, which due to the crosslinking. In order to study the gas adsorption properties of the gas adsorbents synthesized in this experiment, we have measured the adsorption and desorption capacity of nitrogen at 77K. As seen from Figure 4, the adsorption curve of N_2 was well coincided with desorption curve, indicating that N_2 adsorption was almost a physisorption process.

Influence of temperature and pressure on CO_2 adsorption

In order to investigate the characteristics of gas adsorption on the porous composite material EPI/PC-CD, CO_2 adsorption and desorption at 273 and 298K was experimentally measured within the CO_2 pressure range of 0-1bar; and the results are shown in Figure 5. As shown in Figure 5(a), the capacity of CO_2 adsorption on the porous composite adsorbent increased with the increase of CO_2 pressure and temperature. For instance, the capacities of CO_2 adsorption at 298K were significantly affected by CO_2 pressure, which were 5.030 cm^3/g at 0.5bar and 8.613 cm^3/g at 1bar, respectively. The capacity of CO_2 adsorption at 0.5bar declined to 5.030cm^3/g from 1.362 cm^3/g with increasing adsorption temperature from 298K to 273K, indicating that CO_2 adsorption on as-prepared composite adsorbent was an endothermic process and high CO_2 adsorption capacity could be achieved at high temperature. According to the method described in the literature[14,15], the isosteric heat of CO_2 adsorption in Figure 5(b) were between 72 and 78kJ/mol.



(a)



(b)

Figure 5. Isotherms(a) and isosteric heat(b)

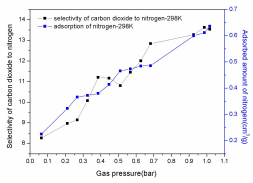


Figure 6 Adsorption selectivity of CO_2 over N_2 at 298K

Selectivity

The selectivity of CO_2 adsorption is very important for the porous composite adsorbent EPI/PC-CD in its application of gaseous phase catalytic synthesis and gas adsorption. Therefore, the behavior of N_2 adsorption was also experimentally investigated and the related results are shown in Figure 6. As seen from Figure 6, the capacity of N_2 adsorption increased slightly with the increase of gas pressure below 1bar and retained below 0.853cm^3/g. For instance, when gas pressure increased from 0.4bar to 0.6bar, the capacity of N_2 adsorption at 298K only increased to 0.379cm^3/g from 0.484cm^3/g, which were much less than that of CO_2 adsorption. For the porous composite adsorbent EPI/PC-CD, the adsorbed molar ratios of CO_2 to N_2 were above 13 at 298K, indicating that high adsorption selectivity of CO_2 over N_2 could be achieved.

Conclusion

A porous composite material derived from pulp cellulose and β-cyclodextrin was successfully prepared and used as CO_2 adsorbent. The adsorption properties of CO_2 were experimentally investigated at different temperatures and gas pressures. In addition, the characteristics of the adsorbent were revealed with the analysis of BET and FTIR. The capacity of CO_2 adsorption at 298K was 8.613cm^3/g at 1bar and adsorption selectivity of CO_2 over N_2 reached above 13, indicating the as-prepared porous composite material could be used as CO_2 adsorbent.

Acknowledgments

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