

CO₂ Capture by Applying Porous Carbon

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ABSTRACT

Carbon dioxide plays a significant role in environmental scale and industrial utilization. As an essential gas in the atmosphere, CO₂ is crucial, however, a predictable trend shows that CO₂ will become excessive, even triggering severe issues to the planet. Some abnormal phenomenons have corroborated the predication and a pragmatic solution is urgently needed. This paper, through research review, gives examples of porous carbons which generally exhibit excellent carbon dioxide uptake capacity. The category of raw material of porous carbon is diverse, and the paper selects reports about porous carbons obtained from different precursors. Their CO₂ uptake capacities are estimated and discussed via some principles such as heat of adsorption, porosity, synergy. The paper finds that all the mentioned porous carbons such as Shrimp shell, Glucose, Sawdust, Date, Phenolic resin, Hyperlinked porous polymer show remarkable CO₂ uptake performance in the investigation. Using porous carbon as approaches of CO₂ adsorption will surely become one of the most prevailing trends in future material development.

Keywords: Porous carbon, CO₂ capture, microporosity, Shrimp shell, Date

1. INTRODUCTION

In recent decades, enormous amount of carbon dioxide has been released into the atmosphere, and its concentration is still continuously increasing. The impact of CO₂ emission is impossible to ignore, which directly results various earthly disasters: glacier reduction, sea level rising, extreme climate, and global warming[3]. According to the U.S. National Oceanic and Atmospheric Administration, the concentration of atmospheric CO₂ will exceed 400 ppm 2016. Now, it is progressing to reach 500 ppm, far higher than the expected concentration of 350-450 ppm that various studies suggested [4-6]. These signs substantiate that handling CO₂ emission is badly urgent. So far, researchers have tried multiple strategies or invented new materials that can relieve the CO₂ in the greatest degree. In order to deal with the issue effectively, researchers need to find the most facilitated and economical solution as a disposition. After years of investigations and experiments, many ideas such as film material, molecular sieve, zeolite, and many more have been explored and assessed, and several exceptional materials and approaches gradually emerge and show extraordinary prospects in CO₂ adsorption. Some well-known sorbents are used for CO₂ adsorption such as zeolite, porous crystalline solid, porous polymer.[1]. One of them, porous carbon, greatly satisfies the criterion that

researchers are aiming for: low cost and convenience[2,8,11]. This raw material to produce porous carbon can be derived easily (biomass, polymer, and etc). In addition, its porosity enhances adsorption to carbon dioxide capture through particular textural properties. These features guarantee the accessibility that porous carbon can pretty be focused as an imperative material. The discovery and exploration to porous carbon has significant meaning that its properties are chosen to be a potential and feasible technology to reduce massive CO₂ emission. Currently, researchers studying on porous carbon are expected to optimize its physical adsorption by testing pore sizes and specific surface area. The alteration of pore size and specific surface area can vary the volume of CO₂ adsorption distinctly. Possibly, these amendments can promote the ability of porous carbon, empowering this material transform from experimental target to be a realistic application.

In this review, CO₂ uptake performance of porous carbon will be researched through experiment. Each type of porous carbon will be made and assessed by the researchers. These investigation results are of great significance, which is convenient for subsequent researchers to preview current understanding about porous carbon before they begin to spend time and energy in this field of study.

2. POROUS CARBONS

The following part will detailedly describe some porous carbons which show advanced CO₂ uptake capacity throughout investigations.

2.1 Shrimp shell

The raw material should be shrimp shell powders that are initially purified before activation. Through series of procedures of impurity elimination, the powders will be carbonized in a comparatively high temperature in a pure N₂ atmosphere. Afterwards, the product would be drenched in KOH solution in certain types of ratios and operations to process to the next step. After drying out, the final product is completed. Based on the experiment procedure, the as-obtained product shows an exceptional CO₂ adsorption capacity as a result of the synergy of excellent porosity and N-content. All products with different variables used during the fabrication exhibit fine reversibility without hysteresis, meaning that the gas adsorption is a not a chemical adsorption, but rather a physical adsorption. In order to improve the CO₂ uptake capacity, adding nitrogen content is pretty important which can greatly enhance the high porosity. There are two pivotal factors that determine the CO₂ uptake ability:

First, high porosity, particularly the large specific surface area and micropore volume, could hold a considerable amount of CO₂ into the production; Second, heteroatom combination as the nitrogen doping, can promote the surface basicity to reinforce the affinity force with acidic CO₂ particles [12-14].

According to the data showed in table 1, the samples are examined in their CO₂ uptake capacity in different temperatures. Statistically, the SAs shows extraordinary CO₂ adsorption capacities of 3.78-6.82 and 2.39-4.20 mmol g⁻¹ at 273 and 298 K and 1 bar, respectively. Conspicuously, SA-1-700 manifests the superior CO₂ uptake of 6.69 and 4.20 mol g⁻¹ at 273 and 298 K, respectively. The CO₂ capture abilities is tightly correlated to micropore sizes compared to other variables such as specific surface area, pore volume, and N content. In distinctive temperatures, CO₂ adsorption capacities are influenced by the micropore size. At 273 K, the micropore(< 1.6nm) is responsible for the CO₂ uptake mainly; at a higher temperature environment of 298 K. A micropores(< 1 nm) is needed to apply into the CO₂ capture. As a result, it is obvious that the narrow micropore is a predominant factor to CO₂ capture and furthermore provides a solution for advanced porous carbon to productive CO₂ capture [15, 16].

Table 1. Data of CO₂ uptake performance in different temperature (CO₂ uptake mmol/g)

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Sample	SA-1-600	SA-1-700	SA-1-800	SA-2-600	SA-2-700	SA-2-800
273k	5.29	6.69	5.28	3.78	6.82	5.03
298k	4.04	4.20	3.22	2.39	3.77	3.06
323k	2.49	2.48	2.05	1.69	2.36	1.94

2.2 Glucose

Furthermore, the porous adsorbent derived from glucose also shows remarkable CO₂ uptake performance.

The first step of glucose-derived porous carbon is to modify the precursor into hydrochar spheres by the uses of cetyltrimethyl ammonium bromide (CTAB) and deionized water(DI). Via series of processes, including stirring, sealing, heating, recollection, etc, the Glucose-based Hydrochar spheres(HSs) are then produced. Afterwards, the HSs were heated and activated by CO₂ flow, cooled down and further mixed with urea in a ratio of 1:1; then, it was heated and dried overnight. The product after the cooling process is denoted as (ACSSs) and the urea treated ACSs were denoted as ACSs-N.

According to the material analysis, the as-obtained product shows promising capacity in adsorption to specific gases. The process of high temperature treatment and urea modification helps shrink the average diameter of the carbon skeleton, eventually reduce the size from

360nm (hydrochar spheres) to 310nm for ACSs (activated porous carbon spheres) and 180nm for ACS-N (urea-treated ACSs). Noticeably, the rougher surface of ACSs-N compared to hydrochar spheres, as a result of CO₂ activation and urea treatment, shows an advantageous influence for the gas diffusion, ranging from different orientations and active site contacts. The analysis structure of the porous carbon suggests the importance of pore size distribution (PSD). The capacity of various porous carbons can be determined by the PSD curves. The difference in procedure can easily be reflected into the PSD curves. Besides, according to the theoretical and experimental results, a narrow PDS gives accommodation place for particles of gases and constrains them within micropores under the Van Der Waals' force.

Furthermore, the concentrated PSD exhibits a prominent ability for similar-sized gas molecule separation. Although the ACSs-N is shown to have a expanded pore size and a lower peak intensity owing to the skeleton collapse and micropore alliance of the

interior of the carbon sphere caused by the urea treatment, it is still being considered as a viable material for gas capture because of the narrow PSD. The chemical proportion is also been analyzed. The analysis verifies the component of the porous carbon and further finds out that the heteroatom N can help improve the selectivity of the adsorption in porous carbon. It meanwhile reinforces the carbon framework polarity [17-20]. Conclusively, the analysis points out two factors shared similar features to the product obtained from the shrimp shell — obtaining a favorable CO₂ uptake capacity: First, microporous structure, particularly the narrow micropores (< 1 nm),

Table 2. Data of CO₂ uptake performances in different pressure (CO₂ uptake mmol/g)

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Sample	CO ₂ uptake (mmol/g)							
	SD2600D	SD2600	SD2700D	SD2700	SD2800D	SD2800	SD4800D	SD4800
0.15 bar	1.3	1.3	1.3	1.3	0.8	0.8	0.5	0.6
1 bar	4.5	4.4	4.6	4.6	3.6	3.6	2.7	3.0
20 bar	10.3	9.7	12.3	12.1	17.5	18.1	21.8	21.7

Another biomass-derived porous carbon is introduced, likewise, the precursor is also a type of substance that can be easily got—sawdust.

A variety of biomass sources will be used in porous carbon synthesis, including eucalyptus wood sawdust, the flowering plant *paenonia lactiflora*, seaweed, etc. For direct activation process, KOH was added into the precursors, and after being heated at a required temperature in the tubular furnace, the carbonaceous material would be obtained and cleaned with HCl, eliminating all impurities with the assist of thermogravimetric analysis. Afterwards, the product will be dehydrated. Meanwhile, conventional fabrication procedure were discussed as well. The sawdust will be transformed into hydrochar through hydrothermal canonization and further being activated by a series of process; finally, the porous carbon is acquired.

Through conventional and direct activation approaches, researchers wanted to ascertain the differences of products obtained from two fabrication approaches, whether that direct-activation had any drawbacks or otherwise. Through investigation, the product made by direct activation has similar pores size and pore channel system to products acquired from conventional approach. Thus, direct activation is testified that has little or no drawback in aspects of the position nature in the carbons. The carbon uptake capacity at 1 bar ranges from 3.6 mmol/g for samples made at 800°C to between 4.4, 4.5, and 4.6 mmol/g for sample made at 600 and 700°C. The performance of directly activated samples resembles to conventional porous carbons; in addition to this, the directly activated porous carbons exhibit an excellent gravimetric CO₂ uptake, the highest ever reported for porous carbons [24-27] [28-41,49]. At 0°C and a pressure of 1 bar, the CO₂ uptake ability can reach up to 7.3 mmol/g with porous carbons made at

gives the ability to contain CO₂ particles into pores; Second, heteroatom incorporation such as the N-doping, elevates the basicity of the surface and enhances the bonding force with acidic carbon dioxide molecules [18,21-23]. It is noted that ACS-N exhibited the best CO₂ uptake ability among rest of the samples: its CO₂ capacity was 3.03 mol g⁻¹ at 25 degree centigrade, 1 bar. Overall, the result has proved the sample ACS-N a viable adsorbent for CO₂ capture.

2.3 Sawdust

700°C, which is at the top tier of heretofore reported porous carbons via a simpler, more economical, and more direct path. In conclusion, the directly activated carbon shows a great capacity in carbon capture, with records of 22 mmol/g at 20 bar and 25°C or 31 mmol/g at 20 bar and 0°C.

2.4 Date

Another type of precursor date, which is also a type of plant, also reveals noticeable CO₂ uptake ability after researching.

For the production stage, the processed date was denoted as FDDS(freeze-dried date sheets). Afterwards, the product was carbonized under high heat and Ar atmosphere. The as-obtained sample is named CDS-x, which CDS and x represent the carbonized FDDS and carbonization temperature respectively. For the activation, CDS-x was mixed with KOH, dried out and was heated. via series of procedure. The product would finally be dried out. According to the discussion, the carbonization temperature has an obvious effect on the pore formation: with lower temperature during the carbonization and activation, products form micropore and mesopore. In comparison, a higher temperature during carbonization and activation favor micropores to form. In reference to the table 3, all AC samples are higher than raw carbon samples when comparing with their CO₂ adsorption capacities. The CO₂ capacities range from 4.07-6.40 and 290-4.36 mmol/g at 0 and 25°C, respectively. The CO₂ uptake abilities of 6.4 mmol/g is noteworthy which outweigh many biomass-derived activated carbon products reported. Researchers also assesses the heats of adsorption in order to understand the binding affinity of the sample. The resultant values show a much lower energy required to break the bond of

CO₂(749 kilojoule/mol). The interactions, therefore, suggest that the interactions between the CO₂ and adsorbents are physisorption process. Porosity also takes a significant factor in CO₂ adsorption ability: the uptake not only closely associates with the pore volume, but also is restricted by the smaller pores; and when the pores have sizes that are two or three times larger than the CO₂ particle(ca. 0.33nm), the adsorption can acquire the optimized energy.[8, 42] Hence, the studies show the pore size around 0.7-0.9nm is the best fit for CO₂ storage,

Table 3. Data of CO₂ uptake performance in different temperature (CO₂ uptake mmol/g)

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Sample	CO ₂ uptake (mmol/g)							
	CDS-500	ACDS-500-2	ACDS-500-4	ACDS-500-6	CDS-800	ACDS-800-2	ACDS-800-4	ACDS-800-6
25°C	1.56	4.18	3.35	2.90	1.88	4.14	4.36	3.65
0°C	1.50	5.98	4.91	4.07	2.40	6.00	6.40	5.60

2.5 Phenolic Resin

Besides biomass-derived porous carbon, the products made from polymers are equally significant as another general genre of precursor in porous carbon fabrication.

The commercial phenolic resins can be identified as a carbon precursor for porous carbon production. For the fabrication process, the polymer needed to be initially carbonized in the reactor with specific conditions. After that, urea modification and KOH activation will be applied along with elaborate procedures and requirements. Until the last step, temperature and mass ratio of KOH/product will be varied and thus produce various forms of porous carbon for further investigation. The carbonized phenolic resins was named as R. Besides, the after-product of R which were modified by urea was denoted as RU. The N-doped carbonaceous sorbents were named as RUK-X-Y(they were applied further activation with KOH under various conditions), the X represents the activation temperature and Y indicates the KOH/RU mass ratio. The variable of temperature included 600°C, 650°C or 700°C and the mass ratio were 2, 3, or 4. These notes has applied into the table 4, as the name of the sample showed.

Noteworthy, RUK-600-3 has the highest CO₂ adsorption capacity of 4.61 mmol/g at 25°C, the highest CO₂ uptake capacity among all the sample; meanwhile, it possesses the second highest Nitrogen content of all adsorbents. RUK-600-4 shows the second-highest CO₂ uptake of 4.58 mmol/g at 25°C, but with a moderate amount of N content. While some of other samples contain the highest value of Vn or N content, respectively, their performances in CO₂ are not as high as the two samples forementioned. This result indicates the synergetic effect of microporosity and N content masters the CO₂ uptake performance at ambient conditions. Furthermore, the pore size and narrow micropores distribution are also two critical factors of a prominent CO₂ uptake performance: large micropore size and wide

micropore size distribution can weaken the capacity of CO₂ uptake. As the porous carbon is tested for its CO₂ adsorption capacity, its ability, up to 4.61 mmol/g at 25°C and 7.13 mmol/g at 0°C under 1 bar, is believed among the best of other known porous carbons, comparing to some adsorbents: zeolites, MOFs, and porous polymers [7,43-46]. As a result, this type of N-doped porous carbon shows an high CO₂ uptake capacity under atmospheric pressure, not only because of its remarkable ability in CO₂ capture, but also its cost effectiveness, qualifying this type of resin-derived porous carbon, a potential candidate for an applicable CO₂ adsorbent in the future.

2.6 Hyperlinked Porous Polymer

Analogously, using hyperlinked porous polymer can also produce high-CO₂-capture porous carbon.

The synthesis using a covalent-organic polymer called COP-M, which can be refer to a Methyl Functionalized Cross-linked Organic polymer. The direct carbonization process needs to put the powder into the container with specific conditions and yield the final product. The yielding rate is 70%. Additionally, the fabrication of KOH mediated carbonization drenches the COP-M powder into the solution based on the weight ratio and mix them well. Afterwards, the mixture will be further proceeded in a high-heated and pure N₂ environment. Last, the product will be cleaned and dried out with a yielding rate of 58%. Based on the experiment discussion, the gas uptake feature of the product is shown to be strong: a KOH activated sample exhibited highest CO₂ adsorption of 7.6 mmol/g at 273k. Furthermore, a conspicuous CO₂ uptake of 6.3 mmol/g at 25°C by another sample, outweighs many amine based sorbents and N-doped carbons [9,47,48]. The benefit of KOH mediated activation is demonstrated by the superior capacity of the product in CO₂ capture. Meanwhile, the mechanism of the adsorption is analyzed according to the heat of adsorption. Among all the samples, one with

higher value in heat of adsorption has a better performance in CO₂ uptake than the one with lower value, which reveals that the heat of adsorption can also be a critical factor that determines the CO₂ uptake capacity. In sum, the COP-M derived porous carbon shows an extraordinarily effective capacity in CO₂ capture.

3. CONCLUSION

In conclusion, the paper gathers some types of porous carbon fabrication. With no exception, all of the porous carbons mentioned in the paper exhibit a promising CO₂ uptake capacity. Some porous adsorbents prominently apply synergy of porosity and N-doped content into the product and largely enhance the carbon dioxide uptake. With the synergistic effect, the microporous structure with N-doped material enables the CO₂ molecule to be accommodated into the pore, enlarging the amount of uptake capacity. Meanwhile, the basicity of the nitrogen-doping facilitates the adsorption which improves the affinity to carbon dioxide via bonding force. Some products also are probed and evaluated during the discussion section, including changing pore size to maximize the potential of CO₂ uptake capacity, and flaws that debase the performance of the products, etc. Some porous carbons reveal remarkable advantages such as environmental friendliness, inexpensive cost, simple or even direct procedure, etc. With a moderate cost and excellent capacity, porous carbon may become one of the most important and promising candidates for environmental improvement, especially in the fields of carbon capture and global warming. Therefore, it has attracted a lot of attention from scholars.

Certainly that some inadequacies also appear in this paper that morphology may also be a critical factor that determines the capacity of CO₂ uptake, but it has not been discussed in this paper. Some improvements should be addressed next time that the author ought to discuss morphology, specific surface area more in detail, and meanwhile keep other contents unchanged. Personally, explorations for future research should be focused on mass application and meanwhile continuing to find some optimal production (including the precursor) solutions of porous carbon, making them viable economically, environmentally, and realistically.

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