



Carbon dioxide adsorption on poly(vinylidene chloride)-based carbons with ultrahigh microporosities prepared by facile carbonization



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ABSTRACT

Poly(vinylidene chloride) (PVDC)-based carbon with high microporosity was prepared via facile carbonization, and further moderate KOH activation can widen micropore size with higher surface area and larger pore volume. A superior CO₂ capture uptake at 1 bar of up to 5.87 mmol/g at 0 °C and 3.98 mmol/g at 25 °C is obtained for pristine carbon and the isosteric heat of CO₂ adsorption is in the range of 24–28 kJ/mol, along with fast kinetics. The KOH activated sample shows a slightly low CO₂ uptake at 1 bar because activation produces some larger micropores in frameworks, resulting in the reduction of interactions between pores and CO₂ molecules.

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1. Introduction

Nowadays, the substantial increase of CO₂ concentration in atmospheric has raised great attention on the global climate change, resulting in worldwide efforts for the reduction of CO₂ emissions. Adsorption for carbon capture and sequestration is probably the most feasible method for decreasing CO₂ emissions in the long run due to its environmental benign, low energy requirement, and easy operation [1–4]. To date, adsorbents for CO₂ capture including carbons, zeolites, metal-organic frameworks (MOFs) and ionic liquids have been widely pursued [5–8]. Among them, MOFs and carbons have gained the most attention. Although high CO₂ capture uptakes of MOFs were reported by some scholars [6], the preparation of MOFs is usually time-consuming and cost-expensive, along with low stability towards water vapor. Therefore, carbons can be considered as promising adsorbents under ambient conditions in view of their large surface areas, good thermal and chemical stability, hydrophobic surface, and viable CO₂-friendly adsorption sites on the pore surface [9–11].

Poly(vinylidene chloride) (PVDC) is a promising precursor for preparing carbons with high performance, and previous studies have confirmed that activation can further enlarge surface area and pore volume [12]. In early researches, PVDC-based carbon was usually studied as separation membrane or electrode materials [13–15]. In this work, the PVDC-based carbon was prepared with wholly micropores via facile carbonization and activation, possessing high surface area and large pore volume. The existence of high microporosities in this carbon motivated us to evaluate CO₂ adsorption properties under ambient conditions. To the best of our knowledge, this is the first time

that such type of material has been explored as an adsorbent to capture CO₂ and shows excellent capture performance at both 0 and 25 °C and ambient pressure.

2. Experimental

The homogeneous PVDC powders (Food grade, Shantou Jincong Food Co., Ltd., China) were used as precursors. Basically, PVDC powders were loaded in a vertical quartz tube (i.d.=16 mm) and heated up to 800 °C at a rate of 5 °C/min under a N₂ flow (80 mL/min) and hold for 3 h. PVDC-based carbon (PC) was obtained after it was ground and sifted with a 400 mesh sieve. Activation was performed by heat-treating the physical mixture of PC/KOH with mass ratio of 1:4. The mixture was treated (2 °C/min) at 800 °C for 1 h under a N₂ flow (80 mL/min). The derived sample washed several times with 2 M HCl solution and copious of water until neutral pH achieved and dried in oven at 120 °C for 10 h and named as AC800-PC.

The phase structure of carbons was studied via X-ray diffraction (XRD, Bruker D8 Advance). Morphology was observed on a scanning electron microscopy (SEM, Hitachi S4800). Pore structure was evaluated via N₂ adsorption at 77 K on a volumetric sorption analyzer (ASAP2020, Micrometrics, USA). The CO₂ capture properties were studied on an Intelligent Gravimetric Analyzer (IGA-001, Hiden) with correction for the buoyancy effect. More details on characterization are shown in the Supporting Information.

3. Results and discussion

The XRD patterns (Fig. 1a) showed that carbons are characterized with a significant content of amorphous phase. There are nearly no sharp diffraction peaks in whole pattern only with two broad and

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weak peaks around at $2\theta=21^\circ$ and 44° , which are ascribed to the (002) and (101) diffraction from turbostratic carbons, respectively [2,15]. Moreover, intensity of peaks in PC is slightly stronger than the one in AC800-PC. The former peak of 21° is hardly recognizable in AC800-PC while can be clearly observed in PC, indicating that the activation can effectively inhibit the graphitization of carbon to some extent. However, the morphology of carbons is not greatly changed after activation even if the electrical conductivity for AC800-PC is slightly poorer than PC during the SEM observation process. Both PC (Fig. 1b) and AC800-PC (Fig. 1c) spontaneously displays disordered and rough surface without layered-graphite structures, which are in excellent agreement with XRD data that PVDC-based carbons are largely amorphous.

N_2 sorption isotherms for PC and AC800-PC and their pore size distribution (PSD) curves are illustrated in Fig. 2. The two isotherms are type-I isotherms and both samples adsorb large amounts of N_2 at low pressures, suggesting a remarkable development of microporosity. The adsorbed amount in AC800-PC is much higher than PC, indicating that activation can largely enlarge surface area and pore volume. BET specific surface area (Fig. S1) and pore volume for PC are respectively up to $1220\text{ m}^2/\text{g}$ and $0.47\text{ cm}^3/\text{g}$. After KOH activation, the surface area and pore volume

for AC800-PC are up to $2150\text{ m}^2/\text{g}$ and $0.9\text{ cm}^3/\text{g}$, which are comparable to some zeolite-templated carbons [2,3]. The isotherms in the low pressure range (Fig. S2) indicate that PC has probably a narrower pore size and larger adsorption enthalpy than AC800-PC, while the activation causes a remarkable uptake of isotherm. It is true that equivalent pore width (Fig. S3) for PC and AC800-PC is around at 1.2 and 1.4 nm, respectively. PSD curves in inset Fig. 2 also indicate that PVDC-based carbons are almost wholly micropores, which are in good agreement with adsorption isotherms. Moreover, PSD curves also confirmed that the activation can widen micropore size in frameworks without seriously wrecking pristine smaller micropores in PC, promoting us to infer that both samples maybe have excellent performance for CO_2 capture under ambient conditions.

At pressures up to 20 bar, CO_2 sorption isotherms of PC and AC800-PC collected 25°C are shown in Fig. 3. Recent reports indicated that carbons with pore size less than 1 nm are very suitable for CO_2 capture under ambient conditions [16], promoting us to study the CO_2 capture performance in PVDC-based carbons. As can be seen from Fig. 3, CO_2 sorption on both carbons was highly reversible without hysteresis and the adsorbed amounts decreased as an increase of temperature (Fig. S4), indicating a physical sorption mechanism [17,18]. Moreover, CO_2 adsorption shows excellent kinetics (Fig. S5). The CO_2 uptakes on PC and AC800-PC at 25°C are separately up to 3.98 and 3.67 mmol/g at 1 bar, while the uptakes at 20 bar are of up to 9.94 and 17.03 mmol/g, respectively. It is worth mentioning that CO_2 uptakes at 1 bar for PC are substantially higher than some of N-containing carbons designed for CO_2 capture [19–21]. Furthermore, the CO_2 uptake at 25°C and 20 bar for AC800-PC is probably in the ranks of the largest capture uptake ever observed for large surface area adsorbent. The superior CO_2 uptake can be ascribed to their excellent pore structures, with large surface areas and high microporosities. Moreover, the isosteric heat (Q_{st}) of CO_2 adsorption (Fig. S6) for PC calculated from isotherms at 0, 10, and 25°C based on the Clausius–Clapeyron equation is in the 24–28 kJ/mol range which is very close to the data reported for other carbons [10,17,18]. The calculated Q_{st} of CO_2 adsorption for AC800-PC also decreases as

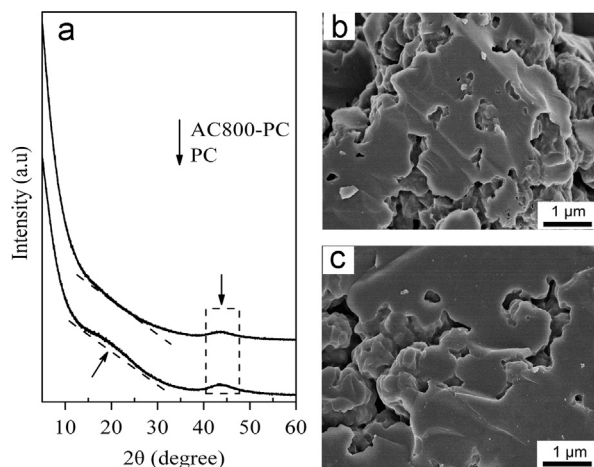


Fig. 1. (a) XRD patterns and (b and c) representative SEM images for PC and AC800-PC respectively.

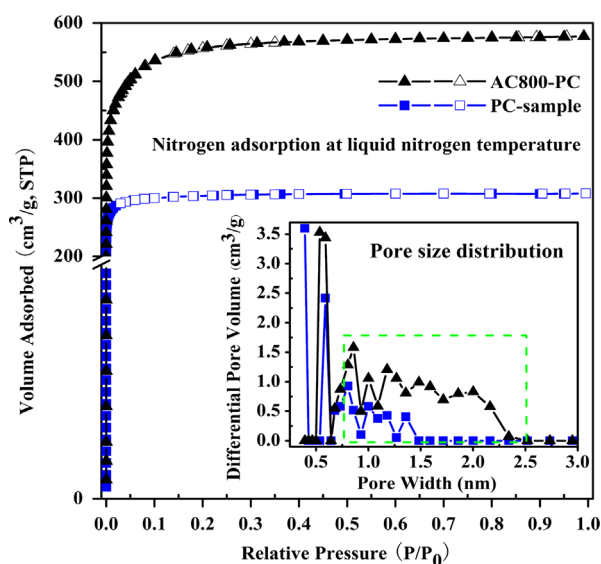


Fig. 2. N_2 sorption isotherms for PC and AC800-PC, and inset is the corresponding pore size distribution (PSD) curves.

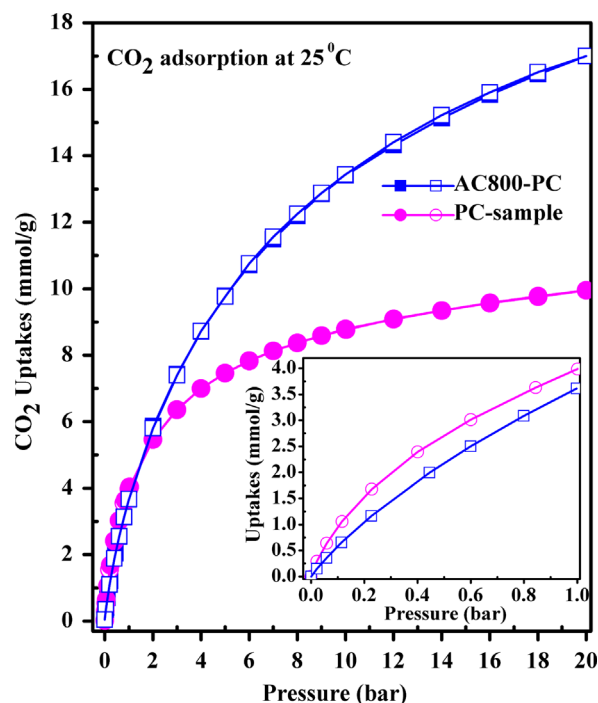


Fig. 3. CO_2 sorption isotherms for PC and AC800-PC at 25°C and 20 bar, and inset is the corresponding adsorption isotherms at 1 bar.

the adsorbed amounts increase, and the value is slightly lower than the one for PC as the adsorbed amounts up to 2.0 mmol/g (Fig. S6). Based on the adsorption results, we can infer that the effective micropore width maybe have larger effect than surface area on CO₂ capture at low pressure while surface area can have a reverse larger effect at high pressure. Generally, CO₂ uptake is greatly dependent on the fraction of ultramicropores (~0.8 nm) at low pressure [11,16]. It is not difficult to illustrate that both AC800-PC and PC show large uptake up to 500 mbar, reflecting the importance of ultramicropores in CO₂ capture at low pressure [22,23]. Therefore, a proper adjustment of microporosity is necessary to enhance CO₂ uptake, namely, carbons with lower surface area but proper microporosity can also have large CO₂ capture capacities.

4. Conclusions

Microporous PVDC-based carbons with superior CO₂ uptake at ambient condition were prepared. The CO₂ uptake reaches 3.98 mmol/g for pristine carbon at 25 °C and 1 bar. KOH activation can greatly enhance the surface area and pore volume, along with small mesopores in framework, showing a superior CO₂ uptake of 17.03 mmol/g at 25 °C and 20 bar. The high CO₂ uptakes are due to the presence of small micropores and ultrahigh microporosity, endowing this kind of carbon to be promising candidate for CO₂ capture.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2013.10.004>.

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