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Poly(vinylidene chloride)-Based Carbon with Ultrahigh Microporosity and Outstanding Performance for CH_4 and H_2 Storage and CO_2 Capture

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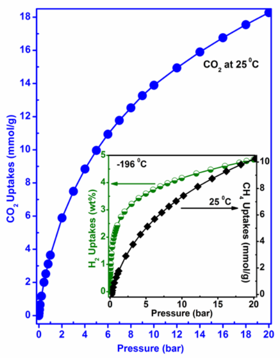
S *Supporting Information*

ABSTRACT: Poly(vinylidene chloride)-based carbon (PC) with ultrahigh microporisity was prepared by simple carbonization and KOH activation, exhibiting great potential to be superior CO_2, CH_4, and H_2 adsorbent at high pressures. The CO_2 uptake for pristine PC is highly up to 3.97 mmol/g at 25 °C and 1 bar while the activated PC exhibits a slightly lower uptake at 1 bar. However, the activated PC has an outstanding CO_2 uptake of up to 18.27 mmol/g at 25 °C and 20 bar. Gas uptakes at high pressures are proportional to the surface areas of carbons. The CH_4 uptake for the activated PC is up to 10.25 mmol/g (16.4 wt % or 147 v/v) at 25 °C and 20 bar which is in a top-ranked uptake for large surface area carbons. Furthermore, H_2 uptake on the activated PC reaches 4.85 wt % at −196 °C and 20 bar. Significantly, an exceptionally large H_2 storage capacity of up to 2.43 wt % at 1 bar was obtained, which is among the largest value reported to date for any porous adsorbents, to the best of our knowledge. The ease of preparation and large capture capacities endow this kind of carbon attractive as promising adsorbent for CH_4, H_2, and CO_2 storage.



KEYWORDS: *porous carbons, carbonization, activation, carbon capture, hydrogen storage*

■ INTRODUCTION

Today, the generation, storage, and delivery of energy source in a renewable and clean fashion may be the largest challenge in our 21st century. Hydrogen is considered to be one of the most attractive energy carriers in the near future for resolving energy-related problems.[1−3] However, how to solve the issue of efficient storage is still the greatest bottleneck to realizing the practical application for hydrogen energy. Several previous studies have demonstrated the potential of physisorption on microporous carbons to realize the Department of Energy (DOE, USA) target of hydrogen storage (5.5 wt % and 0.04 kg/m^3 in 2015); however, many recent works have confirmed again that this technology could meet the DOE target only at cryogenic temperatures.[4,5] Moreover, the combustion of fossil fuels is playing a critical role in rapidly growing concentration of CO_2 in atmosphere, and the emitted CO_2 is one of main resources of greenhouse gas that contributes to 60% of global warming.[6−9] The substantial increase of CO_2 emission in atmospheric has raised enormous attention to the climate change, resulting in a worldwide effort in developing new method on the reduction of CO_2 concentration.[10,11] Moreover, new kinds of renewable and clean energies have also been extensively sought around the world to reduce carbon emissions. The effective H_2 storage in porous carbons is very important in contribution to the ease of our reliance on fossil fuels. Environmental problems caused by the emissions from fossil fuels combustion have created an increasing interest for developing alternative solution based on clean energies. Adsorption is probably the most feasible way to decrease the CO_2 emissions in the long run due to its low energy requirement, easy operation, and low maintenance.[6−13] As a promising alternative to the liquid amine or ammonia absorption, there is increasing evidence to indicate that the solid adsorbents such as carbons, zeolites, silica, metal oxide, polymers, metal-organic frameworks (MOFs), and covalent-organic frameworks (COFs) are excellent candidates for gas storage, recognition, and separation.[14,15] It is hoped that these porous solids might be applied to solve the current climate change and energy shortage crises, especially in relation to CO_2 capture and H_2 or CH_4 storage. Among these porous solids, MOFs and carbons have aroused the most attention as the promising adsorbents for CO_2 capture.[8,9] However, it should be noted that the preparation process for MOFs is usually time-consuming and cost-expensive, along with low stability towards water vapor. Moreover, most of porous materials with physisorption process have negligible CO_2 uptakes at the temperature of up to 30 °C due to their surface chemistry and structural instability. Fortunately, carbons almost encompass all prerequisite attributes for CO_2 capture: high surface area, easy-to-design pores, fast-reversible sorption, hydrophobicity, good stability, ease in regeneration, and viable adsorptive sites on the pore surface.[16−19] There is no doubt that carbons have seized the largest focus on CO_2 capture, even though they have possibly slightly lower uptake compared to other kinds of

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adsorbents. In addition, application of inexpensive carbons instead of MOFs would help to decrease the material costs and then steer the development of adsorbents.[20]

On the other hand, natural gas has potential to replace petroleum as the world's primary fuel for transportation. CH_4 as the main component of natural gas has received a sustainable attention as the future energy source due to its natural abundance, relative safety with respect to most other fuels, low cost, and low carbon emissions.[21,22] A significant increase has been witnessed in the production of natural gas as an environmentally clean fuel supply, in view of sharp increase in the oil prices and stringent environmental regulation. How to storage CH_4 at mild conditions is very important for the economic and engineering development. Up to now, different methods are known for on-board natural gas storage such as liquefied, compressed, and adsorbed natural gas.[21] However, expensive cost associated with design and manufacture of liquid CH_4 containers in the case of liquefied natural gas, and difficulty related to the high pressures in the case of compressed situation have indicated that adsorption has become a promising alternative for effective CH_4 storage. Furthermore, the most important advantage is that the moderate high-density CH_4 storage can be achieved at relatively mild condition with adsorption storage method, viz., ambient temperature and moderate pressure (30−60 bar).[23,24] The success of adsorption method largely relies on the development of new kinds of porous adsorbents such as carbons with superior characteristics, possessing large surface areas, good stabilities, and low costs, tuned for these specific applications.

Polymer-based carbons with high surface areas and porosities have been largely studied in recent years.[10,18,25−28] Importantly, poly(vinylidene chloride) (PVDC) is one of promising precursors for preparing porous carbon with high performance as the separation membrane or electrode material.[29−32] A comprehensive study in activating this kind of precursor to carbons with high surface area and large pore volume, and the subsequent performance in gas storage has not been reported yet. Recently, Xu et al.[33] have demonstrated that the activation of the PVDC-based carbons using NaOH as activators have good electrochemical capacitance. The determination of gas storage performance of adsorbents especially for high pressures is very significant to both the development of new adsorbents and the evaluation of suitability of an adsorbent in practical application. Here, we report the preparation of PVDC-based carbons by simple carbonization and moderate KOH activation, possessing high surface area (up to 2150 m^2/g) and pore volume (up to 0.9 cm^3/g). Significantly, carbons possess high microporosity in these pores which will be definitely positive effects in gas storage. To explore its potential applications on greenhouse gas adsorption and separation, adsorption isotherms of CH_4/CO_2 were collected at pressures up to 20 bar. Furthermore, H_2 storage performance on this kind of carbon was also evaluated at −196 °C and 20 bar. Results indicated that PVDC-based carbons are promising adsorbents for energy-related gas storage. To the best of our knowledge, this is the first time that such type of carbon was used as adsorbent to study the capture performance of energy-related gases at high pressures.

■ EXPERIMENTAL SECTION

Reagents and Carbon Preparation. Homogenous PVDC powders (Food grade, Shantou Jincong Food Co., Ltd. China) were used as precursor. The detailed preparation process for carbons can be found elsewhere.[31,32] Basically, PVDC powders were carbonized in a vertical quartz tube (i.d. = 16 mm) and heated to 800 °C at a rate of 5 °C/min under N_2 flow (80 mL/min) and hold for 3 h, and the obtained black product was named as PC. Later, partial PC powders were ground with KOH pellet with special mass ratios in an agate mortar for post-activation treatment. The mixtures were transferred into the same vertical furnace and heated up to 800 °C for 1 h under N_2 flow at a heating rate of 2 °C/min. The obtained products washed several times with 2M HCl solution and copious of water until a neutral pH was achieved and then dried at 120 °C for 10 h. The final black product was denoted as ACn-PC, where "AC" refers to "activation", and "*n*" refers to the mass ratio between KOH and PC.

Characterization of Carbons. The structural features of carbons were studied via X-ray powder diffractometer (XRD, Bruker D8 Advance) and confocal laser Raman spectrometer (LabRAM HR UV-NIR, Jobin Yvon). The morphology of carbons was observed on a scanning electron microscopy (SEM, Hitachi S4800). The pore structures were characterized by N_2 sorption on a static volumetric sorption analyzer (ASAP2020, Micrometrics). Before adsorption measurements, all samples were degassed for 10 h at 200 °C under high vacuum.

Gas Adsorption Measurements. Gas adsorption measurements were carried out on an Intelligent Gravimetric Analyzer (IGA, Hiden), which is an ultrahigh vacuum system, and incorporates a microbalance capable of measuring weight with a resolution of ±0.1 μg. Gases used in experiments (CO_2, CH_4, and N_2) were provided by Heli Gas Co., Ltd., China with high purity (99.999%). Ultrahigh purity (99.9999%) of H_2 and high purity (99.95%) of D_2 were further purified with activated carbon, alumina, and zeolite to remove trace amount of water and other impurities before introduction into IGA system. Water adsorption was also performed on the same IGA system at pressures up to 6 mbar and then gas was immediately changed to CO_2 for the humid CO_2 adsorption at l bar with a relative humidity of around 18.8% after water adsorption reached equilibrium at 6 mbar. All adsorption results were corrected for buoyancy effect with the corrected parameters indicated in previous works.[5,34,35] Before adsorption measurement, samples were degassed (1×10^{-6} bar) at 200 °C for 5 h, with a heating rate of 1 °C/min.

■ RESULTS AND DISCUSSION

The XRD patterns and SEM images for PVDC-based carbons were separately illustrated in Figures S1 and S2 (see the Supporting Information). It can be found from the XRD data in Figure S1 in the Supporting Information that carbons are characterized with a significant content of amorphous phase in the structures, and the graphitization degree of carbons was very poor. There're nearly no sharp diffractions only with two broad and weak peaks around at 21 and 44°, which is ascribed to the (002) and (101) plane from turbostratic carbon, respectively.[30,32] Moreover, the weak peak of 21° in AC2-PC and AC4-PC happens to be completely disappeared, and the relative intensity for the peak of 44° in AC2-PC and AC4-PC is slightly weaker than the one in the pristine PC, indicating that KOH activation treatment can moderately inhibit the graphitization of carbon to some extent. On the other hand, the SEM images of carbons in Figure S2 in the Supporting Information display a disordered and rough surface without obvious layered-graphite structures, which are in good agreement with XRD data that PVDC-based carbons are largely amorphous. However, SEM image for AC2-PC in Figure S2 in the Supporting Information shows an appearance with some melted state and evident difference from PC and AC4-PC, reflecting the complex process in activating carbons. In addition, Raman spectra in Figure S3 (see the Supporting Information) indicated that two strong peaks around at 1596 cm^{-1} (G band) and 1347 cm^{-1} (D band) existed in the carbons, attributing to the C−C bond vibration of carbon atoms in graphite layer with sp^2 electronic configuration and imperfect structure of the carbons, respectively.[36] Moreover, the intensity ratio of I_D/I_G between the two bands is larger than 0.95, confirming their abundant defects and poor graphitization. The observed decrease of I_D/I_G in these carbons indicates that numbers of sp^2-bonded carbon atoms without dangling bond have increased at the expense of disordered carbons.[37]

To investigate the effect of KOH activation on the pore structure of carbons, we measured N_2 sorption isotherms for carbons, and their corresponding pore size distributions (PSDs) were illustrated in Figure 1. Physical properties including the Brunauer−Emmet−Teller (BET) surface areas and pore volumes of the carbons were summarized in Table 1. According to the IUPAC classification,[38] the resulting N_2 adsorption isotherms in Figure 1a for carbons were typical type-I isotherms that adsorbed large numbers of N_2 molecules at relative low pressure range ($P/P_0 < 0.05$), after which adsorption levels off with further increase of relative pressure, indicating that these carbons are essentially microporous. In general, the smoother adsorption isotherms are, the more micropores exist in carbons, and vice versa. N_2 adsorption isotherms in Figure 1a also indicate that the KOH activation can greatly increase the adsorbed amounts, showing an enlargement of surface area and pore volume of carbons. Furthermore, the KOH activation will also moderately widen the isotherm knee of carbons to some extent which is an indication of generating some large micropores or small mesopores in carbon framework.[1,28] Importantly, N_2 isotherms of the carbons seem to reach a horizontal plateau above $P/P_0 \approx 0.2$, indicating that the carbons have ultrahigh microporosity and mesoporosity is practically little or non-existing. The ultrahigh microporosity in this kind of carbon indicates that both the appropriate selection of raw material and activation process are very important in determining the ultimate performance of carbons. Importantly, adsorption properties could be tuned by changing the activation condition, which was proved by the different adsorbed amounts of N_2 in Figure 1a. A semilogarithmic plot of N_2 isotherms differentiated adsorption behavior for PC and AC4-PC at low pressure range in Figure S4 (see the Supporting Information) indicate that PC has probably a narrower micropore size and larger adsorption enthalpy than AC4-PC,[18,39] even though KOH activation causes a remarkable uptake of isotherms. It is well-known that excessive activators for the post-activation process will definitely cause micropores to widen in the mesopore ranges due to the breakage of pore walls between adjacent micropores.[28,29,40−42] However, carbons with high proportion of mesopores while equal surface areas will not greatly benefit for the gas storage performance, to the best of our knowledge. Therefore, the situation of N_2 adsorption isotherms and PSD curves for two samples (AC6-PC and AC8-PC) obtained from higher concentration of activators were shown in Figure S5 in the Supporting Information and not discussed in the main text. As shown in Table 1, KOH activation for carbons does result in a decrease in the microporosity while an increase in total pore volume. The calculated BET surface area and total pore volume for PC are up to 1220 m^2/g and 0.47 cm^3/g, respectively. After KOH activation, however, surface area and total pore volume for AC4-PC are highly up to 2150 m^2/g and 0.90 cm^3/g, respectively. All the changes are probably due to this activation process opening some closed pores, excavating some new

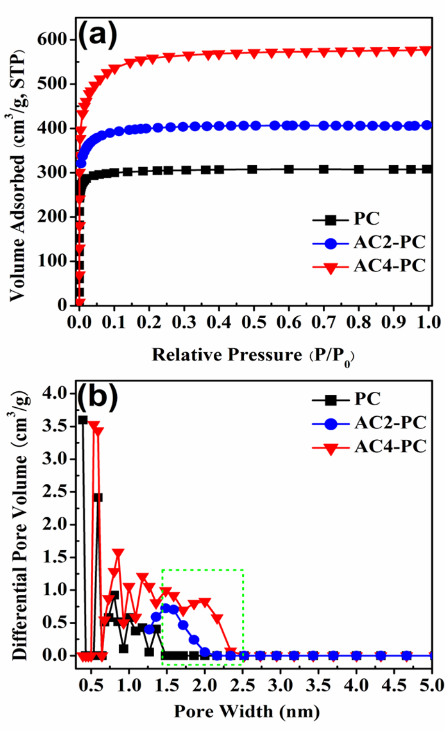

Figure 1. (a) N_2 adsorption isotherms, and (b) pore size distributions (PSDs) of carbons obtained from applying the density functional theory (DFT) method to adsorption data.

Table 1. Textural Properties of the PVDC-Based Carbons Derived from N_2 Adsorption Data at −196 °C, and the Capture Uptakes of CO_2 and CH_4 at 25 °C and Elevated Pressures

samples	S_{BET} (m^2/g)[a]	V_{Total} (cm^3/g)[b]	V_{Micro} (cm^3/g)[c]	D_R[d]	density (g/cm^3)	CO_2 (mmol/g)		CH_4 uptake at 20 bar	
						1 bar	20 bar	(mmol/g)	(v/v)
PC	1220 (1328)	0.47	0.47	1.29	0.88	3.97	10.56	7.15	141
AC2-PC	1598 (1559)	0.63	0.60	1.32	0.77	3.69	13.94	8.53	147
AC4-PC	2151 (2095)	0.90	0.85	1.44	0.64	3.64	18.27	10.25	147

[a] The surface areas are calculated from Brunauer−Emmet−Teller method at P/P_0 = 0.01−0.05, and values in parentheses are micropore surface areas obtained from Dubinin-Astakhov (DA) equation. [b] The total pore volumes are estimated from the adsorption data of N_2 at p/p_0 = 0.996. [c] Micropore volumes are determined via the DA method. [d] Average pore width of carbons is obtained via the DA method.

narrow micropores, and widening some pre-existent pores.[43] The detailed calculations for the surface areas are shown in Figure S6 (Supporting Information). BET surface areas of the present carbons are slightly inferior than the previous reports using NaOH as the activators,[33] resulting from the different activation mechanisms. PSD curves in Figure 1b have also indicated the existence of high proportion of micropores in the carbons which are in excellent agreement with N_2 adsorption isotherms in Figure 1a. Moreover, the little difference between BET surface areas and micropore surface areas in Table 1 also suggests high microporosity of this kind of carbon. It is very apparent that all pores in the pristine PC are less than 1.5 nm whereas KOH activation widens partial micropores to 2.5 nm for the AC4-PC. Despite this evident tendency to large micropores and small mesopores, however, both the AC2-PC and AC4-PC still retain most of microporosity. Very importantly, all the average pore sizes of these carbons in Table 1 are less than 1.5 nm, indicating the ultrahigh microporosity of carbons. Some recent studies have indicated that the small micropores less than 1.0 nm are very important in the application of greenhouse gas capture under ambient condition.[20,31,44−48] The PVDC-based carbons reported in this work are largely possible to have superior CO_2 and CH_4 capture performance because KOH activation greatly enhances surface areas, micropore volumes, and total pore volumes while moderately enlarges micropore size in the framework without seriously wrecking the small micropores in the pristine PC. The presence of high microporosity in these carbons motivated us to examine their potential application in the areas of greenhouse gas capture and separation.

The CO_2 adsorption performance on the carbons at 25 °C and 20 bar are illustrated in Figure 2 and the detailed uptakes are listed in Table 1. Although the AC2-PC and AC4-PC have much larger surface area and pore volume than the pristine PC, it can be observed from Table 1 and Figure 2 that CO_2 uptake on the carbons at 1 bar is slightly decreased after KOH activation. The CO_2 uptakes at 1 bar and 25 °C collected for the pristine PC are up to 3.97 mmol/g, which is substantially larger than some of polymers, MOFs, and N-containing activated carbons designed for the CO_2 capture.[8,10,12,18,25,28,49−54] However, we have to admit that the present CO_2 uptakes are still slightly lower than some activated carbon spheres and carbon molecular sieves under the same conditions,[55−57] suggesting the importance of proper selection of raw materials and activation process on the ultimate adsorption performance. The detailed comparative results of CO_2 uptake at 25 °C and 1 bar between the pristine PC in this work and adsorbents reported in literature were listed in Table 2. This excellent CO_2 capture performance for PC under ambient conditions makes it to be a more promising candidate for the following adsorption studies. We believe that activation generates some large micropores or small mesopores in the framework, and then results in the reduction of interaction between adsorbates and pore walls.[31,48] Combined with the PSD curves in Figure 1b, we firmly believe that the superior CO_2 uptakes at 1 bar for the PC are mainly due to the presence of large quantities of micropores less than 1.0 nm, reflecting the importance of small micropores in CO_2 capture at low pressures.[20,44−47,57,58] However, adsorption isotherms of CO_2 at 25 °C and 20 bar in Figure 2 indicate that the CO_2 uptake for AC2-PC and AC4-PC largely exceeds the one in pristine PC as pressure gradually increases, wholly proportional to the surface areas of samples. Significantly, the CO_2 uptakes at 20 bar for AC4-PC with surface area of 2150 m^2/g reach a value up to 18.27 mmol/g, which is probably one of the largest uptakes ever observed for high-surface-area carbons. No saturation in the isotherms is observed as pressure up to 20 bar, indicating that higher uptake can be even achieved at higher pressure. Considering a fact that the maximum pressure of the IGA system used here is only limited up to 20 bar, and we introduce dual-site Langmuir model to simulate CO_2 adsorption at 25 °C and higher pressure. The dual-site Langmuir model has been

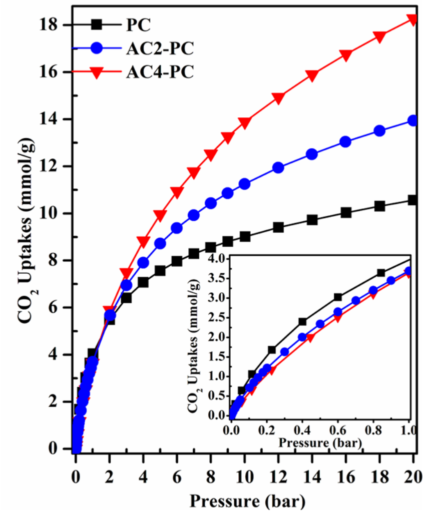

Figure 2. Adsorption isotherms of CO_2 on the carbons at 25 °C and the pressures up to 20 bar, and the inset is the corresponding adsorption at 25 °C and 1 bar.

Table 2. Comparative Results for the CO_2 Capture Properties of Different Adsorbents

adsorbents	CO_2 uptake at 25 °C and 1 bar (mmol/g)	refs
poly(vinylidene chloride)-based carbon (PC)	3.97	this work
zeolite-templated carbon (YTC7)	2.36	7
polyindole nanofibers (PIF-6)	3.20	10
nitrogen-enriched activated carbon (AC)	2.05	12
poly(benzoxazine-co-resol)-based carbon	3.30	18
imine-linked polymer (ILP)	1.95	25
nitrogen-doped polyimine-based carbons	3.10	28
chromium(iii)-based coordination polymer	3.8 (at 0 °C)	49
nitrogen-doped micro-carbon (N-TC-EMC)	4.00	50
melamine-formaldehyde resin-based carbon	2.25	52
nitrogen-doped hollow carbon nanospheres	2.67	53
ordered mesoporous carbon (OMC)	2.87	54
carbon molecular sieve (VR-93-M)	4.59	55, 56
carbon molecular sieve (VR-5-M)	4.20	56
activated carbon spheres (CS-6-CD-4)	4.55	57
carbon foam	2.51	58

widely used to analyze CO_2/CH_4 capture properties at high pressure for MOFs and carbons.[59,60] As shown in Figure S7 in the Supporting Information, the model can be well-used to describe the experimental CO_2 data on AC4-PC with the correlation coefficient (R^2) of 0.9999 and the simulated CO_2 uptake at 25 °C and 40 bar is highly up to 22.13 mmol/g or 97.37 wt %, which is almost equivalent to the value reported on zeolite-templated carbon with surface area 3010 m^2/g.[61]

On the other hand, it is very interesting to note that CH_4 adsorption on the carbons at 1 bar in Figure S8 in the Supporting Information shows an analogous trend to the situation of CO_2 adsorption. To explore the potential application of these carbons in CH_4 storage, adsorption isotherms of CH_4 on carbons at 25 °C and 20 bar were provided in Figure 3. As can be observed from Figure 3a, AC4-PC shows the largest CH_4 uptake of up to 10.25 mmol/g (16.4 wt %) at 25 °C and 20 bar due to its large surface area and pore volume. In general, the capture uptake in adsorbent systematically increases with increasing porosity while the gas storage pore occupancy will slightly decrease with increasing pore size.[22,24] The gravimetric CH_4 uptake in Figure 3a is also proportional to the surface area of carbons. Importantly, the volume adsorbed amounts of CH_4 for both the AC2-PC and AC4-PC in Figure 3b at 25 °C and 20 bar reach the value up to 147 v/v, which is in the top-ranked storage capacities ever observed for large surface area carbons,[22,62−65] to the best of our knowledge, exhibiting the great potential for the KOH activation of carbons in applications for natural gas capture. It is not difficult to understand the large CH_4 uptakes for AC2-PC and AC4-PC that many studies have confirmed that the most effective pores for CH_4 capture are these larger micropores around at 1.5 nm,[63,65−67] and PSD curves in Figure 1b for AC2-PC and AC4-PC are fortunately located in this range. Moreover, adsorption levels for CH_4 at the relative high pressures in AC4-PC can keep increasing due to condensation effect in the space available within large micropores or small mesopores. It should be noted that the situation for the volume adsorbed amounts is not quite similar to the gravimetric one, where the pristine PC exhibits larger uptakes than AC2-PC and AC4-PC as the pressure less than 10 bar, even if the pristine PC possesses much lower surface area. As shown in Figure S9 in the Supporting Information, the dual-site Langmuir equation is well adopted to describe CH_4 adsorption data on AC4-PC with the correlation coefficient (R^2) of 0.99998. Significantly, the simulated CH_4 uptake on the AC4-PC at 25 °C and 35 bar is highly up to 12.53 mmol/g (20.05 wt % or 179 v/v), which is very close to the target of 180 v/v set by DOE.[68] Furthermore, the simulated CH_4 capacity at 50 bar is highly up to 13.85 mmol/g, corresponding to the value of 22.16 wt % or 199 v/v. It is important to emphasize that while dual-site Langmuir model describes CO_2/CH_4 adsorption data very well over wide pressure ranges; however, other models maybe also result in equally good or in some cases perhaps even better, fits to the data. Based on the adsorption result, we can infer that the effective micropore size may have a larger effect than surface area on gas adsorption at low pressures, whereas surface area can have a reverse larger effect at relative high pressures. KOH activation for carbons can largely increase surface area and pore volume, and therefore inevitably results in the enlargement of gas uptake at higher pressures.

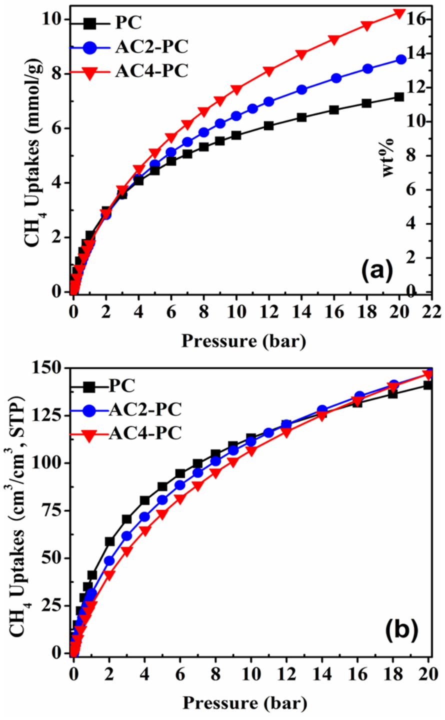

Figure 3. Adsorption isotherms of CH_4 on the carbons at 25 °C and 20 bar: (a) molar uptakes vs. pressure, and (b) volume uptakes vs. pressure.

To evaluate the CO_2 separation performance for this kind of carbon, we collected single-component CO_2, CH_4, and N_2 adsorption isotherms for PC at 25 °C and 1 bar in Figure 4a. Moreover, water adsorption and humid CO_2 adsorption on PC were also performed (see Figure S10 in the Supporting

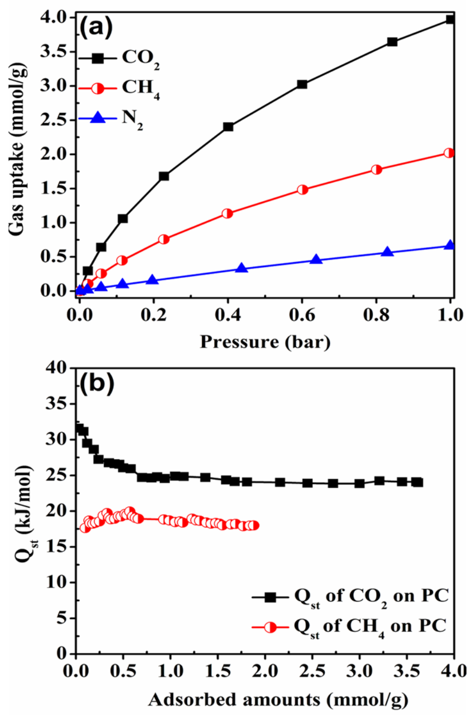

Figure 4. (a) Selective adsorption of CO_2 over CH_4 and N_2 for the PC at 25 °C and 1 bar, and (b) the isosteric heat of CO_2 adsorption on the PC calculated from adsorption data at different temperatures based on the Clausius−Clapeyron equation.

Information). We can find that the adsorbed amounts of water are very small at low pressure, and the humid environment has little effect on the following CO_2 adsorption, indicating hydrophobic characteristics of surface for the carbon.[16] It is apparent that PC has better adsorption uptakes for CO_2 in view that it can adsorb up to 1.9 times more CO_2 than CH_4 at 1 bar. The different adsorption behaviors can be partially because of molecule size of adsorbates, where CO_2 molecule has a little smaller kinetic diameter than CH_4, allowing CO_2 molecules easy access to large proportion of microporosity in the carbons.[69] Both the adsorbed CO_2/CH_4 amounts for carbons shown in Figure S11 in the Supporting Information gradually decrease as an increase of temperature, confirming the nature of physisorption mechanism. Comparatively, PC has a very small N_2 uptake about 0.65 mmol/g and isotherms of N_2 are quite linear compared with the situation of CO_2/CH_4 isotherms, suggesting weak interactions between the guest N_2 molecules and pores. We can speculate that the PC has probably a moderate selectivity for CO_2/N_2 and CH_4/N_2. In general, the ideal selectivity can be determined by applying a linear fit to the isotherms at low pressures (below 0.2 bar) and later calculating the relative ratio of slopes.[54,70] We believe that this method provides a suitable measurement of selectivity at the pressure appropriate for flue gas application where the CO_2 partial pressure will be much less than 1 bar. The initial slopes of CO_2, CH_4, and N_2 isotherm is calculated to be 10.83, 4.38, and 0.86, respectively, and the selectivity for CO_2/N_2 mixture gas is 12.59, suggesting that this kind of PVDC-based carbon has moderate selectivity towards CO_2 when compared with other kinds of adsorbents.[6,10,51,54] Therefore, next surface modification is very necessary to further improve CO_2/N_2 selectivity in future work.

Apart from the capture uptakes for the adsorbents, isosteric heat (Q_{st}) of adsorption is an important indicator for the regenerability of an adsorbent. Importantly, the Q_{st} is always taken into account to estimate the temperature effect during adsorption. The energetic heterogeneity of surface for an adsorbent can be also evaluated via comparison of the Q_{st} value.[6] Combined with the adsorption performance of CO_2 and CH_4 in Figures 2 and 3, respectively, the Q_{st} of CO_2 and CH_4 adsorption on the pristine PC as an example were calculated based on the Clausius-Clapeyron equation using the adsorption data at different temperatures. The results were shown in Figure 4b and the detailed calculation procedure for the Q_{st} was illustrated in Figure S12 (Supporting Information). As illustrated in Figure 4b, the calculated Q_{st} value for CH_4 adsorption on the PC is in the 17−20 kJ/mol range, and the value is gradually prone to plateau off as the adsorbed CH_4 amounts increase. On the other hand, we have noted that the Q_{st} value for the CO_2 adsorption in the PC initially decrease, and then almost exhibit stable at around 24 kJ/mol with the increase of the adsorbed CO_2 amounts. Importantly, the initial Q_{st} of CO_2 adsorption in the PC is highly up to 32 kJ/mol. The trends in the Q_{st} value for both the CO_2 and CH_4 adsorption suggest that the micropores in the carbon are occupied first and then reach a saturation level after certain amounts of gas uptake. Moreover, both the Q_{st} values for CO_2/CH_4 adsorption in this kind of carbon are slightly larger than those reported on ordered mesoporous carbons (e.g. 18.2 and 15.4 kJ/mol for CO_2 and CH_4, respectively),[6] and some activated carbons (e.g.27.7-20.3 kJ/mol for CO_2),[54,57] presumably because of the narrower pores in these carbons, indicating the relatively strong interactions between gas molecules and pore walls of carbons.

H_2 adsorption performance on the carbons was investigated at −196 °C and pressures up to 20 bar, and the results were shown in Figure 5. Furthermore, we validated the observed adsorption uptake was due to H_2 rather than other impurities through the measurement of D_2 isotherms on the same IGA system. Comparative adsorption isotherms for H_2/D_2 on the PC as an example were collected over the range of 0−1 bar at −196 °C and shown in Figure S13 in the Supporting Information. It is expected that the mass ratio of the adsorbed D_2/H_2 is close to 2:1, and the corresponding molar ratio is around at 1.02, which are excellent consistent with those values observed in our previous data on other kind of microporous adsorbents.[3,5,71,72] H_2 uptakes on PC, AC2-PC and AC4-PC are up to the values of 3.23, 4.11, and 4.85 wt %, respectively. It is very obvious that adsorption trend for H_2 uptake is proportional to the surface area of carbons. Although H_2 storage uptake of 4.85 wt % for AC4-PC is still at a relatively inferior situation compared to some previous reported data on zeolite-templated carbons and carbon mesotubes,[5,73−75] the reported value is larger than most other kind of activated carbons.[4,49] It is true that a recent evaluation of H_2 uptake over a wide range of high surface area activated carbons has observed a maximum uptake of 4.5 wt % even at much higher pressures.[74] On the other hand, H_2 uptake at -196 °C and 1 bar for AC4-PC in Figure 5b is exceptionally up to 2.43 wt %, which is among the largest uptake reported in literatures for any adsorbents, to the best of our knowledge. The situation for H_2 adsorption in the kind of PVDC-based carbon is in line with the monolayer adsorption mechanism proposed by the group of Zhou et al.[76] It is suggested that the small micropores in the 0.6−0.9 nm range are the most effective for H_2 storage.[4,76,77] Therefore, we believe that the comparative high H_2 uptake for carbons in this work is related to their ultrahigh microporosity.

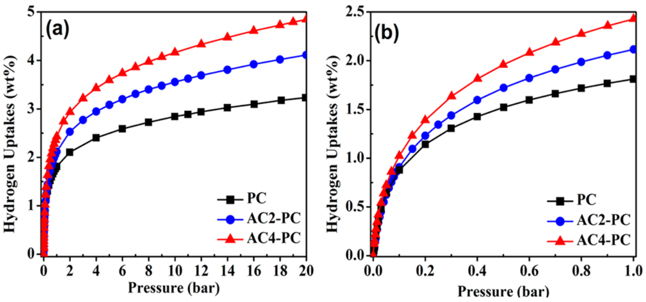

Figure 5. H_2 adsorption isotherms for the PVDC-based carbons at 77 K and pressures up to: (a) 20 bar, and (b) 1 bar.

■ CONCLUSIONS

The PVDC-based carbons with large surface area and ultrahigh microporosity were prepared by simple carbonization and KOH activation. The pristine PC has no pores larger than 1.5 nm and the activated AC2-PC has no pores larger than 2.0 nm. Our results highlight an important topic and provide vision for the development of microporous carbons that have been largely unexplored. It is very exciting that the pristine PC sample shows a superior CO_2 uptake of up to 3.97 mmol/g at 25 °C and 1 bar, and the activated AC4-PC exhibits an exceptionally large H_2 uptake of 2.43 wt % at −196 °C and 1 bar, which is among the largest value of H_2 storage reported in the literature for any adsorbents, to the best of our knowledge. Moreover, the CH_4 uptake reported in this work is up to 10.25 mmol/g (16.4

wt % or 147 v/v) at 20 bar and 25 °C for the activated AC4-PC, which is also in a top-ranked uptake for high surface area carbons. Taking into account the ease of preparation procedure and large uptakes for the carbons, this kind of PVDC-based carbon constitutes a promising adsorbent for CO_2, CH_4, and H_2 storage. However, next surface modification is necessary to further improve the CO_2/N_2 selectivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures for BET plots, XRD patterns, SEM images, Raman spectra, N_2, and water isotherms at low pressures, fitting dual-site Langmuir model, CO_2/CH_4 isotherms at 1 bar, van't Hoff plots, and the comparison of H_2/D_2 isotherms. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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