Evidence for CO₂ reactive adsorption on nanoporous S- and N-doped carbon at ambient conditions

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ABSTRACT

CO₂ interactions with nanoporous S- and N-doped polymer-derived carbon and commercial wood-based carbon were investigated in a broad range of conditions. The results showed that during CO₂ adsorption nitrogen and sulfur species as well as water were released from the carbon surface as a result of chemical reactions of the surface groups with CO₂. Inelastic neutron scattering experiments provided the unprecedented ability to characterize very small amounts of CO₂ and H₂O and revealed for the first time their physical/chemical status in the confined space of nanoporous carbons. The results obtained suggest that the reactivity of the carbon surface should be considered when CO₂ storage media are chosen and when CO₂ is used as a probe to determine the microporosity of carbon materials.

1. Introduction

Global warming is associated with a release to the atmosphere such gases as CH_4 or CO_2 [1, 2]. The atmospheric concentration of CO_2 gradually increases and nowadays it reaches ~ 390 ppmv [3, 4]. One of the methods that have been investigated for a CO_2 capture is based on an adsorption process. As adsorbents, zeolites [5, 6], functionalized mesoporous silica [7, 8], carbon nanotubes [9, 10], metal oxides [11, 12], Metal Organic Frameworks (MOFs) [2, 13-15] or aminated graphite oxides and their composites with Cu-based MOF [16], and activated carbons [17-31] have been tested. One of major finding was an increase in CO_2 adsorption capacity caused by an introduction of basic groups, such as amines, to adsorbent surfaces [7, 8, 32, 33]. Thus in the case of carbon-based adsorbents the effects of nitrogen functional groups providing basicity have been investigated [24-26, 31, 32].

Even though the variety of adsorbents including new materials such as MOF have been explored, traditional adsorbents such as activated carbons and activated carbon fibers are still in a focus of various research groups. It is owing to their high surface area and well-developed porosity [34], and a relative easiness of their surface modifications due to a carbon matrix reactivity, especially at elevated temperatures [35].

In summary of important findings on the factors affecting the CO_2 adsorption capacity on activated carbons their volume of pores smaller than 1 nm, or smaller than 0.7 nm [17-20, 23], comes as a crucial feature, especially when the adsorption process takes place at ambient conditions. This is a consequence of an enhanced adsorption potential in pores similar in their sizes to the CO_2 molecule (0.33 nm) [2, 17-20, 29]. A well-known activation with KOH is often applied for various carbon precursors to develop such porosity [17, 20, 23, 36]. This process

leads to carbons with surface areas over $2600 \text{ m}^2/\text{g}$ [17, 20-22] on which 4.55 mmol/g CO_2 was adsorbed at 1 bar and 25°C [22]. Other studies indicated adsorption of 3.5 mmol/g [17], 4.8 mmol/g [17, 23], and 4.4 mmol/g [20] at the same conditions. Wickramaratne and Jaroniec adsorbed 8.9 mmol/g at 0°C and ambient pressure on their activated carbon spheres [21]. The researchers mentioned the importance of the volume in pores with sizes less than 0.7 nm [17-19, 20, 23]. The summary of recent results on the CO_2 adsorption on various carbonaceous adsorbents is presented in references [36-38].

Modification of carbons with nitrogen functionalities introduces some basicity [24, 32, 33, 39], which is supposed to enhance surface interactions owing to the slightly acidic nature of CO_2 [24]. On such carbons the adsorption capacities for CO_2 ranging from 2.3 mmol/g to 6.2 mmol/g at 0°C have been reported [24, 25, 40]. Interesting finding regarding adsorption of CO_2 on nitrogen containing carbons was presented by Xing and coworkers, who suggested that for CO_2 adsorption on such materials hydrogen bonding might play a more important role than acid-base interactions [26].

Since hydrogen bonding or polar interactions of CO_2 within the carbon pore can originate from other functional groups than those amine-based, recently adsorption of CO_2 on sulfur doped carbons have been addressed [27, 28, 41]. Such carbons have been also investigated as catalysts [42-46] or in energy related fields [47-51]. Thus Xia and coworkers reported the heat of CO_2 adsorption of 59 kJ/mol at low coverage on sulfur doped carbon obtained within the structure of zeolite EMC-2 [27]. Seema and coworkers linked the high capacity for CO_2 adsorption on chemically activated reduced-graphene oxide/poly-thiophene (4.5 mmol/g at 25°C and at ambient pressure [28]) to the “oxidized S-content”, to the presence of pores similar in size to CO_2 molecule, and to the developed surface area of $\sim 1600 \text{ m}^2/\text{g}$. No specificity about the role of

sulfur was provided. Recently, the enhanced adsorption of CO₂ on sulfur containing nanoporous/graphene composites was linked directly to sulfur incorporated to aromatic rings [41]. It has been shown that such configurations enhance CO₂ adsorption via acid-base interactions in micropores. Moreover, sulfonic acids, sulfoxides and sulfones were found as attracting CO₂ via polar interactions and hydrogen bonding. On these materials a very high degree of pore space utilization for CO₂ was found. This is a desired feature since it is rather more important how efficiently this pore volume is used in the adsorption process than how large is it [52].

Based on these recent findings addressing CO₂ adsorption on nanoporous carbons, the objective of this paper is a further and detailed analysis of the interactions of carbon dioxide with the surface of sulfur and nitrogen doped carbons. For this study, the carbon derived from poly (ammonium-4-styrenesulfonate) was used. To broaden the spectrum of surface properties the carbonized polymer was activated in air. The photoactive properties of such carbons have been already reported and linked to sulfur and nitrogen functionalities [53, 54]. Dynamic CO₂ adsorption was studied with simultaneous analysis of the gases released during the process. To gain detailed information on the role of surface chemistry the high-resolution XPS analyses of the carbons' surfaces was carried out before and after the CO₂ exposure. Moreover, the interactions of CO₂ have been studied using inelastic neutron scattering (INS), which was made possible by use of the high-flux, high-resolution neutron vibrational spectrometer (VISION) recently commissioned at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) [55]. We emphasize that our objective is not to evaluate the specific carbons as CO₂ storage media, but to indicate that CO₂ can chemically interact with the surfaces of some carbons and thus the stability of adsorbents in a long-term application can be affected. Additionally, this

reactivity can lead to false results when CO₂ is used as a fine probe to determine the volume of very small pores in some carbons.

2. Experimental

2.1. Materials

The polymer-derived carbon was obtained by carbonization of poly(ammonium-4-styrenesulfonate) in nitrogen at 800 °C for 40 min (N₂ flow rate of 300 mL/min and heating rate of 50 °C/min). The carbonization yield was 40 % and it decreased to about 35 % after water washing. Oxidized carbon, denoted as C-AO, was obtained by heating polymer-derived carbon in air at 350 °C for 3 hours. In order to investigate the importance of specific surface chemical features on the adsorption of CO₂ the commercial wood-based activated carbon, BAX (BAX-1500, Mead Westvaco), was also studied.

2.2. Methods

2.2.1. Dynamic CO₂ adsorption

Assessment of the CO₂ adsorption on our samples was carried out using a TA instrument (SDT Q 600). About 20 mg of the adsorbent was placed in a small pan, heated up to 120 °C at a heating rate of 10 °C/min under pure N₂ flow (100 mL/min) and held isothermally for 3 hours. The temperature was then decreased to 30 °C. Then the gas was switched to pure CO₂ (50 mL/min). The sample was held isothermally at 30 °C for 2 hours. The weight increase during this stage was considered as the CO₂ capture. During dynamic CO₂ adsorption, the composition of gases was monitored by mass spectrometry (OMNI StarTM). Comparison of this data with that obtained at the same condition on unexposed carbon allowed us to track the changes in surface chemistry during CO₂ adsorption.

2.2.2. *CO₂ adsorption isotherms*

CO₂ adsorption isotherms were measured using an ASAP 2020 analyzer (Micromeritics, Norcross, GA, USA) under low pressure (0~0.12 MPa). The experiments were conducted at 0 °C and 30 °C by the Dewar flask using ice water or circulated water in which the sample tube was immersed. Prior to each adsorption experiment, the samples were degassed at 120 °C overnight to constant vacuum (10^{-4} Torr). The reversibility of the CO₂ adsorption process on the samples studied was tested by two CO₂ adsorption cycles. The corresponding adsorption isotherms have been acquired after heating at 120 °C for 12 hours in vacuum in sequence.

2.2.3. *Heats of CO₂ adsorption*

Heats of CO₂ adsorption were measured using the Calvet type DSC (calorimetric detector-3D sensor) (Setaram Instrumentation, Caluire, France). First, the sample was heated up to 120 °C at a heating rate of 10 °C/min under N₂ flow (100 mL/min) and held isothermally for 2 hours. The temperature was then decreased to 30 °C at a rate of 10 °C/min. Then pure CO₂ (50 mL/min) was passing through the sample isothermally with a continuous flow of N₂. The heat flow over time curve was recorded. The heat of CO₂ adsorption in J/g of carbon was calculated by integration of the peaks.

2.2.4. *Evaluation of porosity*

Adsorption of nitrogen at its boiling point was carried out using ASAP 2020 (Micromeritics, Surface Area and Porosity Analyzer). Before the experiments, samples were outgassed at 120 °C to constant vacuum (10^{-4} Torr). The surface area, S_{BET} , (Brunauer-Emmet-Teller method was used), whereas for the volume of pores smaller than 0.7 nm, $V_{<0.7 \text{ nm}}$, micropore volume, V_{mic} , and mesopore volume, V_{meso} , the 2D-NLDFT approach was applied [56]. The volume of mesopores, V_{meso} , represents the difference between total pore and micropore volume. The total

pore volume was calculated from the last point of the isotherm at relative pressure equal to 0.99. The pore size distributions were calculated using two-dimensional nonlocal density functional theory 2D-NLDFT (www.NLDFT.com) assuming heterogeneous surface of pore walls [56].

2.2.5. X-Ray photoelectron spectroscopy (XPS)

The chemical characterization of the surface of the carbon samples was studied before and after CO₂ adsorption. This sample was deposited on a sieve plate (10 mm diameter, 1 mm depth) that allows the reaction gas to pass through the powder. The product gases leave the reaction chamber through an exhaust pipe under the sample. The carbon sample was exposed to 100% pure CO₂ flow at 0.24, 0.5 and 1.0 MPa of pressure with 2h of stabilization time at each pressure. A Physical Electronics spectrometer (PHI 5700) was used, with X-ray Mg K α radiation (300 W, 15 kV, 1253.6 eV) as the excitation source. High-resolution spectra were recorded at a take-off angle of 45° by a concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV, using a 720 μ m diameter analysis area. Under these conditions, the Au 4f_{7/2} line was recorded with 1.16 eV FWHM at a binding energy (BE) of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2p_{3/2}, Ag 3d_{5/2}, and Au 4f_{7/2} photoelectron lines at 932.7, 368.3, and 84.0 eV, respectively. Charge referencing was done against adventitious carbon (C 1s, 284.8 eV). Samples were set in a membranes mounted on a sample holder without adhesive tape and kept overnight at high vacuum in the preparation chamber before being transferred to the analysis chamber of the spectrometer for the testing. Each spectral region was scanned several sweeps up to a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 5×10^{-6} Pa. PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using

Gauss-Lorentz curves and following the methodology described in detail elsewhere [57] in order to determinate more accurately the BE of the different element core levels. Atomic concentration percentages of the characteristic elements of the surfaces were determined taking into account the corresponding area sensitivity factor [57] for the C 1s, O 1s, N 1s and S 2p spectral regions.

2.2.6. Inelastic neutron scattering (INS)

INS was measured at BL16-B (VISION), Spallation Neutron Source (SNS), located at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. The C-AO sample was first wrapped in Al foil, and then loaded in a cylindrical stainless steel high pressure cell that is rated for 69 bar and 315 °C. The pressure cell was then mounted on a gas-handling sample stick. The sample was pumped in vacuum at 120 °C overnight before loading in the CCR to measure at base temperature (5 K). After collecting the INS data for 12 hours on the blank sample, the sample was taken out of the CCR for CO₂ dosing. The sample cell was loaded with 5.3 mmol of CO₂ and immediately cooled to base temperature for measurement. Solid CO₂ was detected in the INS spectra, and the sample was then heated back to room temperature to pump off the extra CO₂. 2.8 mmol of CO₂ was released, with the remaining CO₂ in the cell. After holding at room temperature for about 1 hour, the sample was cooled again to base temperature. INS data was collected for 12 hours on the reacted sample.

3. Results and discussion

Even though some surface properties of the carbons studied here were addressed in details elsewhere [53], we repeated all surface analyses for the new batches of materials used in this study. It was done to assure that even the finest surface details will be taken into consideration in

our exploration of CO₂ (reactive) adsorption. As seen from Fig. 1a, C-AO can be considered an ultramicroporous carbon with the majority of the volume distributed among pores smaller than 0.7 nm (0.215 cm³/g vs total pore volume of 0.363 cm³/g). These pores, as stated in the literature [17-20, 23], play the main role in CO₂ physical adsorption. Adsorption in these small pores should be the predominant mechanism of CO₂ retention in both carbons tested in this work. These interactions will not be discussed further below. We focus on the reactive adsorption, which on some carbons might accompany the physical adsorption phenomenon. BAX carbon, on the other hand, has about half pore volume in pores smaller than 0.7 nm (0.086 cm³/g) and a high volume of mesopores (0.871 cm³/g). Its BET surface area is 2021 m²/g while that of C-AO is almost three times less, 727 m²/g. Although the importance of the surface chemistry of activated carbon has been mentioned in some recent works as playing a potentially significant role in CO₂ adsorption [26, 28, 32, 40, 41], the majority of the work to date emphasizes the predominant role of small pores in the physical adsorption process.

Fig. 1. a) Pore size distributions; b) CO₂ adsorption isotherms; c) The comparison of the CO₂ adsorption capacity measured at equilibrium at 0.01 MPa and 0.1 MPa; and d) Heat flow curves for CO₂ adsorption (the values of the integrated heats of CO₂ adsorption are included in the Figure).

Adsorption of CO₂ on both carbons was measured at 0 °C and 30 °C (Fig. 1b) and the amounts adsorbed at equilibrium are compared at 0.01 MPa, where ultramicropores should be most active, and at 0.1 MPa where micro/mesoporosity might play a role (Fig. 1c). At both temperatures and at low pressure the amount adsorbed on C-AO is almost twice of that adsorbed on BAX. This reflects the difference in the volume of ultramicropores and indicates the predominance of physical adsorption. At higher pressure and low temperature the amounts adsorbed are almost

equal. Interestingly, at 30 °C C-AO outperforms BAX. This reversal in terms of amount of CO₂ adsorbed with an increase in the temperature is a first indication of the higher reactivity of this carbon surface with CO₂. In fact, if the surface groups are chemically active, their effect should be seen at higher pressures since they exist preferentially in pores larger than 0.7 nm. In pores less than 0.7 nm only sulfur or nitrogen groups incorporated to an aromatic ring of the carbon matrix can exist. Examples are pyridine and quaternary nitrogen or sulfur in thiophenic configurations. Much more heat was released from the surface of C-AO than from that of BAX when the heat flow during CO₂ adsorption was measured (Fig. 1d).

To further investigate the interactions of CO₂ with the surface of the studied carbons, we measured the adsorption of CO₂ at 30 °C under dynamic conditions with simultaneous analyses of the off-gases using mass spectrometry. The adsorption profiles are collected in Fig. 2a. CO₂ adsorbs in larger amounts on C-AO carbon compared to BAX. Even though in the off-gases m/z fragments representing CO₂ were detected predominantly (Fig. S1 of Supporting Information), identifying other m/z fragments related to the release of nitrogen and sulfur species was of paramount importance for our analysis (Fig. 2b-d). At the beginning of the adsorption process nitrogen is released from the surface of both carbons and the highest intensity is found for the C-AO carbon at the first contact with CO₂. Afterward the profiles for both carbons look similar. Since nitrogen is present in air at large concentration, this result might be indicative not only of chemical reactions involving CO₂ and nitrogen containing species, but it might also represent the replacement of adsorbed N₂ by CO₂. The latter hypothesis cannot be supported using the balanced amounts of the adsorbed and desorbed species since N₂ adsorption at ambient conditions is very difficult to measure precisely. Nevertheless, when the initial carbons were exposed to helium at 30 °C N₂ was not detected. This can either support the former hypothesis or

indicate that helium is not able to replace adsorbed nitrogen. An increase in the extent of sulfur release is observed only for C-AO during almost the entire adsorption time until CO₂ saturation is reached. The fact that the sulfur is continuously released indicates ongoing surface reactions. Even though the CO₂ gas used for the experiments was dry and the carbons were extensively dried, some water is detected in the off gasses from both samples, and once again the highest signal is found for C-AO. The water signal follows the trend observed for sulfur species in C-AO carbon. It is important to mention that both carbon samples were treated at the same conditions as those used for the CO₂ adsorption experiments (dried) and were exposed to helium flow at 30 °C for the same amount of time as that of CO₂ exposure and no release of nitrogen or sulfur species, or water was detected at 30 °C. Therefore, these results provide a clear indication of the existence of surface reactions taking place during CO₂ exposure. The involvement of nitrogen (to some extent) and especially sulfur functional groups in these reactions is clear. In fact, the release of water in the case of BAX might also suggest involvement of other oxygen-containing groups, including perhaps phosphorous (H₃PO₄ was used for activation), in reactions with CO₂.

Fig. 2. a) The isothermal (30 °C) CO₂ adsorption profiles and b-d) *m/z* thermal profiles recorded during CO₂ adsorption for the materials studied.

We used XPS analysis to evaluate the changes in the carbon surface chemistry upon CO₂ exposure at various pressures. Elemental analysis and the summary deconvolution of the relevant core energy levels are collected in Table 1 and in Fig. 3, respectively. The detailed assignments of the C 1s, O 1s, N 1s and S 2p core energy level spectra are presented in Fig. 4 and Table S1 of Supporting Information. The surface chemical composition of C-AO shows a very slight increase in the percentage of the concentration of C with applied CO₂ pressure, but this increase is not very significant. The deconvolution of C 1s core energy level spectra indicates an increase in carbon as CO, which might be the result of the CO₂ reduction. In the case of the surface concentration of oxygen, a noticeable increase in O-C/O-S bonds (decrease in O=C/O=S)

supports the existence of oxidation reactions on the surface. The O 1s spectrum also shows an increase in the contribution of oxygen from water, which supports the TA-MS results. Clearer variations in the surface concentrations of N and S are observed with increased CO₂ pressures. The observed decrease in the content of nitrogen can be due to the interactions of CO₂ with basic N-containing groups. This might result in a partial coverage of more external N containing groups. The study of the high-resolution core level spectra helps us to find more evidence for the interactions of CO₂ with the surface functional groups. The N 1s core level spectra show very interesting modifications with CO₂ pressure. The contribution at 400.0-400.7 eV, with N in amides, increases from 50.90 to 100 %, and the contribution due to amine groups simultaneously decreases. This fact also explains the observed decrease of the nitrogen content after applying CO₂ pressure, as stated above. This clearly shows the occurrence of an oxidation process. The deconvolution of the S 2p core level spectra after applying CO₂ pressure indicates that the contribution percentages at low binding energy (163.8 eV) gradually decrease. Simultaneously, the percentage of oxidized sulfur-containing species increases and S(VI)-containing species are found (contribution at 168.3 eV). Even though for BAX carbon (Table S2 and Figure S2 of Supporting Information) much smaller changes in surface chemistry are found, the changes in nitrogen are consistent with those observed in C-AO, and oxidation of the surface is observed with a marked decrease in the nitrogen content with an increase in CO₂ pressure. The recording of relatively high amounts of water during CO₂ adsorption, even though this carbon does not have sulfur, might be related to the low level of aromatization of the carbon and an involvement of aliphatic moieties in the reactions with CO₂.

Table 1. Content of elements on the surface (in at. %).

Sample	C	O	N	S
C-AO	81.86	15.47	2.08	0.59
CO ₂ 0.24 MPa	82.21	15.42	1.73	0.65
CO ₂ 0.5 MPa	82.80	15.04	1.44	0.73
CO ₂ 1.0 MPa	81.30	16.02	2.02	0.66
BAX	90.52	9.17	0.31	ND
CO ₂ 0.5 MPa	91.52	8.13	0.35	
CO ₂ 1.0 MPa	90.62	9.20	0.18	

ND – not detected

Fig. 3. Surface concentration the specific carbon, oxygen, nitrogen and sulfur functionalities present on the carbon surface.

Fig. 4. C 1s, O 1s, N 1s and S 2p core energy levels for the polymer-derived activated carbon (C-AO).

We used INS to further analyze the CO₂ interactions with C-AO. The sample was initially loaded with 5.3 mmol of CO₂ and immediately cooled to base temperature (-268 °C) for INS measurements. In the spectrum showing the difference before and after dosing (the black curve in Fig. 5) one can clearly see the characteristic peak of CO₂ at 80 meV (bending mode). The overall spectrum resembles the one measured for bulk solid CO₂ (green curve), suggesting that the predominant amount of CO₂ adsorbed is present as unreacted solid. The sample was then heated up to room temperature to pump off the extra CO₂, with approximately 2.5 mmol of CO₂ left in the sample holder for adsorption/reaction. After holding at room temperature for about 1 hour and cooling back to base temperature, the difference spectrum (red curve) now shows both the bending mode of CO₂ (peak at 80 meV) and the characteristic spectrum of water/ice (comparing with the blue curve which was measured for bulk ice-Ih). This indicates that the sample has reacted with CO₂, and the detection of H₂O in the INS spectrum as a product of the reaction is also consistent with our mass spectrometry result. Even though we consider this as the most important finding of this research, there are other interesting features in this spectrum. First, unlike the black curve with 5.3 mmol of solid CO₂, the translational mode for solid CO₂, that is the mode between 11 and 18 meV present in the spectrum of the unreacted sample and in the solid CO₂ sample spectrum, seems to be missing (or is significantly suppressed) in the red curve. The very sharp peak near 12 meV is mainly due to an artifact caused by elastically scattered neutrons with $\lambda/2$ wavelength. This shows that the remaining CO₂ after the reaction with the sample surface is no longer in the solid state, but is most likely adsorbed on the surface of the sample with limited CO₂-CO₂ intermolecular interaction or has reacted. Second, the librational edge of H₂O measured in the sample is less sharp, and appears shifted towards higher energy compared to that measured in bulk ice. This means the water molecules in the sample are

subjected to stronger restrictions imposed by their interactions in the pore system. One possible explanation is that water interacts strongly with some surface groups, leading to the blue shift the librational band. The ability to characterize very small amounts of CO_2 and H_2O (especially CO_2 which has relatively a low neutron scattering cross-section), and reveal their physical/chemical status with INS, is unprecedented and was only made possible by the high-flux and high-resolution of the VISION instrument. The blank C-AO sample was also measured before dosing, and the INS spectrum is shown as the inset of Fig. 5. The presence of C-H bonds is demonstrated by the strong peak at 390 meV that corresponds to the C-H stretching mode. Several broad bands between 100 and 200 meV correspond to C-H bending modes [58].

Fig. 5. The difference INS spectra before and after CO_2 dosing in C-AO, in comparison with the reference spectra for bulk solid CO_2 and H_2O . Signal from the background and the blank CAO has been subtracted. Inset shows the INS spectrum of the blank C-AO before dosing (note that the energy scale is different).

4. Conclusions

The results collected in this study for the first time show that CO_2 interacts chemically with the surface groups of our S- and N- doped carbon samples. There is also an evidence for chemical reactions of CO_2 with the surface of a commercial carbon (BAX) upon CO_2 adsorption. The data suggest that sulfur and nitrogen in the reduced forms are oxidized when exposed to CO_2 . One plausible mechanism of these interactions is CO_2 reduction either to CO or to formic acid. In fact nitrogen-containing carbons are known for their activity to reduce CO_2 in electrochemical processes [59]. It is possible that in the small pores electrons are transferred from nitrogen in pyridine forms, and sulfur in thiophenic configurations to CO_2 resulting in oxidation of nitrogen and sulfur species and in the release of some of them as N_2 and SO. The results indicate that water is a byproduct of these reactions. Some CO and CO_2 could also be released. Since CO_2 is an adsorbate, both CO_2 and CO cannot be detected using the dynamic adsorption measurements. Notice that the release of CO can result in a subtle activation of a carbon surface. Even though some reactivity of CO_2 at ambient conditions with the carbon surfaces was detected, the predominant mechanism of its retention in the carbon pore system is physical adsorption. Nevertheless, when carbons are chosen as CO_2 sequestration media based on cyclic operation and when CO_2 is used as a probe to determine the fine porosity of carbonaceous adsorbents caution is advised based on the possible existence of chemical reactions between carbon dioxide and residual N and S functional groups at the pore surface.

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References

1. Hansen J, Johnson D, Lacis A, Lebedeff, S, Lee P, Rind D, et al. Climate impact of increasing atmospheric carbon dioxide. *Science* 1981;213:957-66.
2. D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: Prospects for new materials. *Angew Chem Int Ed* 2010;49:6058-82; *Angew Chem* 2010;122:6194-219.
3. Yang H, Xu Z, Fan M, Gupta R, Slimane RB, Bland AE, et al. Progress in carbon dioxide separation and capture: A review. *J Environ Sci* 2008;20:14-27.
4. Samanta A, Zhao A, Shimizu GKH, Sarkar P, Gupta R. Post-combustion CO₂ capture using solid sorbents: A review. *Ind Eng Chem Res* 2012;51:1438-63.
5. Kim J, Lin L-C, Swisher JA, Haranczyk M, Smit B. Predicting large CO₂ adsorption in aluminosilicate zeolites for postcombustion carbon dioxide capture. *J Am Chem Soc* 2012;134:18940-3.
6. Fang H, Kamakoti P, Ravikovitch PI, Aronson M, Paur C, Sholl DS. First principles derived, transferable force fields for CO₂ adsorption in Na-exchanged cationic zeolites. *Phys Chem Chem Phys* 2013;15:12882-94.
7. Zukal A, Jagiello J, Mayerova J, Cejka J. Thermodynamics of CO₂ adsorption on functionalized SBA-15 silica. NLDFT analysis of surface energetic heterogeneity. *Phys Chem Chem Phys* 2011;13:15468-75.
8. Yu J, Le Y, Cheng B. Fabrication and CO₂ adsorption performance of bimodal porous silica hollow spheres with amine-modified surfaces. *RSC Adv* 2012;2:6784-91.
9. Hsu S-C, Lu C, Su F, Zeng W, Chen W. Thermodynamics and regeneration studies of CO₂ adsorption on multiwalled carbon nanotubes. *Chem Eng Sci* 2010;65:1354-61.

10. Cinke M, Li J, Bauschlicher Jr. CW, Ricca A, Meyyappan, M. CO₂ adsorption in single-walled carbon nanotubes. *Chem Phys Lett* 2003;376:761-6.
11. Broda M, Müller CR. Synthesis of highly efficient, Ca-based, Al₂O₃-stabilized, carbon gel-templated CO₂ sorbents. *Adv Mater* 2012;24:3059-64.
12. Wang Q, Tay HH, Zhong Z, Luo J, Borgna A. Synthesis of high-temperature CO₂ adsorbents from organo-layered double hydroxides with markedly improved CO₂ capture capacity. *Energy Environ Sci* 2012;5:7526-30.
13. Liu J, Thallapally PK, McGrail BP, Brown DR, Liu J. Progress in adsorption-based CO₂ capture by metal–organic frameworks. *Chem Soc Rev* 2012;41:2308-22.
14. Qian J, Jiang F, Yuan D, Wu M, Zhang S, Zhang L, et al. Highly selective carbon dioxide adsorption in a water-stable indium–organic framework material. *Chem Commun* 2012;48:9696-8.
15. Millward AR, Yaghi OM. Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. *J Am Chem Soc* 2005;127:17998-9.
16. Zhao Y, Seredych M, Zhong Q, Bandosz TJ. Aminated graphite oxides and their composites with copper-based metal-organic framework: in search for efficient media for CO₂ sequestration. *RSC Adv* 2013;3:9932-41.
17. Sevilla M, Fuertes AB. Sustainable porous carbons with a superior performance for CO₂ capture. *Energy Environ Sci* 2011;4:1765-71.
18. Zhang Z, Zhou J, Xing W, Xue Q, Yan Z, Zhuo S, et al. Critical role of small micropores in high CO₂ uptake. *Phys Chem Chem Phys* 2013;15:2523-9.
19. Martín CF, Plaza MG, García S, Pis JJ, Rubiera F, Pevida C. Microporous phenol-formaldehyde resin-based adsorbents for pre-combustion CO₂ capture. *Fuel* 2011;90:2064-72.

20. de Souza LKC, Wickramaratne NP, Ello AS, Costa MJF, da Costa CEF, Jaroniec M. Enhancement of CO₂ adsorption on phenolic resin-based mesoporous carbons by KOH activation. *Carbon* 2013;65:334-40.
21. Wickramaratne NP, Jaroniec M. Importance of small micropores in CO₂ capture by phenolic resin-based activated carbon spheres. *J Mater Chem A* 2013;1:112-6.
22. Wickramaratne NP, Jaroniec M. Activated carbon spheres for CO₂ adsorption. *ACS Appl Mater Interfaces* 2013;5:1849-55.
23. Silvestre-Albero J, Wahby A, Sepulveda-Escribano A, Martinez-Escandell M, Kaneko K, Rodriguez-Reinoso F. Ultrahigh CO₂ adsorption capacity on carbon molecular sieves at room temperature. *Chem Commun* 2011;47:6840-2.
24. Zhou J, Li W, Zhang Z, Xing W, Zhuo S. Carbon dioxide adsorption performance of N-doped zeolite Y template carbons. *RSC Adv* 2012;2:161-7.
25. Sevilla M, Valle-Vigón P, Fuertes AB. N-doped polypyrrole-based porous carbons for CO₂ capture. *Adv Funct Mater* 2011;21:2781-7.
26. Xing W, Liu C, Zhou Z, Zhang L, Zhou J, Zhuo S, et al. Superior CO₂ uptake of N-doped activated carbon through hydrogen-bonding interaction. *Energy Environ Sci* 2012;5:7323-7.
27. Xia Y, Zhu Y, Tang Y. Preparation of sulfur-doped microporous carbons for the storage of hydrogen and carbon dioxide. *Carbon* 2012;50:5543-53.
28. Seema H, Kemp KC, Le NH, Park S-W, Chandra V, Lee JW, et al. Highly selective CO₂ capture by S-doped microporous carbon materials. *Carbon* 2014;66:320-6.
29. Jimenez V, Ramirez-Lucas A, Diaz JA, Sanchez P, Romero A. CO₂ capture in different carbon materials. *Environ Sci Technol* 2012;46:7407-14.

30. Sevilla M, Fuertes AB. CO₂ adsorption by activated templated carbons. *J Colloid Interface Sci* 2012;366:147-54.
31. Sevilla M, Parra JB, Fuertes AB. Assessment of the role of micropore size and N-doping in CO₂ capture by porous carbons. *ACS Appl Mater Interfaces* 2013;5:6360-8.
32. Hao G, Li W, Qian D, Lu A. Rapid synthesis of nitrogen-doped porous carbon monolith for CO₂ capture *Adv Mater* 2010;22:853-7.
33. Li Q, Yang J, Feng D, Wu Z, Wu Q, Park SS, et al. Facile synthesis of porous carbon nitride spheres with hierarchical three-dimensional mesostructures for CO₂ capture. *Nano Res* 2010;3:632-42.
34. Gregg SJ, Sing KSW. Adsorption, Surface Area, and Porosity, New York, Academic Press, 1982.
35. Bandosz TJ, Ania CO. Surface chemistry of activated carbon and its characterization. In: Bandosz TJ, editor. *Activated carbon surfaces in environmental remediation*, Oxford: Elsevier; 2006. p. 159-230.
36. Martin-Jimeno FJ, Suarez-Garcia F, Paredes JI, Martinez-Alonso A, Tascon JMD. Activated carbon xerogels with a cellular morphology derived from hydrothermally carbonized glucose-graphene oxide hybrids and their performance towards CO₂ and dye adsorption. *Carbon* 2015;81:137-147.
37. Tesng, R-L, Wu F-C, Juang R-S. Adsorption of CO₂ at atmospheric pressure on activated carbons prepared from melamine-modified phenol-formaldehyde resins. *Sep Purif Technol* 2015;140:53-60.

38. Diez N, Alvarez P, Granda M, Blanco C, Santamaria R, Menendez R. N-enriched ACF from coal-based pitch blended with urea-based resin for CO₂ capture. *Micro Meso Mater* 2015;201:10-6.
39. Deng S, Wei H, Chen T, Wang B, Huang J, Yu G. Superior CO₂ adsorption in pine nut shell-derived activated carbons and the effective micropores at different temperatures. *Chem Eng J* 2014;253:46-54
40. Chandra V, Yu SU, Kim SH, Yoon YS, Kim DY, Kwon AH, et al. Highly selective CO₂ capture on N-doped carbon produced by chemical activation of polypyrrole functionalized graphene sheets. *Chem Commun* 2012;48:735-7.
41. Seredych M, Jagiello J, Bandosz TJ. Complexity of CO₂ adsorption on nanoporous sulfur-doped carbons – Is surface chemistry an important factor? *Carbon* 2014;74:7-217.
42. Kicinski W, Szala M, Bystrzejewski M. Sulfur-doped porous carbons: Synthesis and applications. *Carbon* 2014;68:1-32.
43. Liang J, Jiao Y, Jaroniec M, Qiao SZ. Sulfur and nitrogen dual-doped mesoporous graphene electrocatalyst for oxygen reduction with synergistically enhanced performance. *Angew Chem Int Ed* 2012;51:1-6; *Angew Chem* 2012;124:11664-8.
44. Seredych M, Bandosz TJ. Confined space reduced graphite oxide doped with sulfur as metal-free oxygen reduction catalyst. *Carbon* 2014;66:227-33.
45. Petit C, Kante K, Bandosz TJ. The role of sulfur-containing groups in ammonia retention on activated carbons. *Carbon* 2010;48:654-67.
46. Seredych M, Bandosz TJ. Adsorption of dibenzothiophenes on nanoporous carbons: Identification of specific adsorption sites governing capacity and selectivity. *Energy Fuels* 2010;24:3352-60.

47. Bandosz TJ, Matos J, Seredych M, Islam MSZ, Alfano R. Photoactivity of S-doped nanoporous activated carbons: A new perspective for harvesting solar energy on carbon-based semiconductors. *Appl Catal A: Gen* 2012;445-446:159-65.
48. Seredych M, Bandosz TJ. Effect of the graphene phase presence in nanoporous S-doped carbon on photoactivity in UV and visible light, *Appl Catal B: Environ* 2014;147:842-50.
49. Zhao X, Zhang Q, Chen C-M, Zhang B, Reiche S, Wang A, et al. Aromatic sulfide, sulfoxide, and sulfone mediated mesoporous carbon monolith for use in supercapacitor. *Nano Energy* 2012;1:624-30.
50. Seredych M, Bandosz TJ. S-doped micro/mesoporous carbon/graphene composites as efficient supercapacitors in alkaline media. *J Mater Chem A* 2013;1:11717-27.
51. Seredych M, Singh K, Bandosz TJ. Insight into the capacitive performance of sulfur-doped nanoporous carbons modified by addition of graphene phase. *Electroanalysis* 2014;26:109-20.
52. Seredych M, Kosciński M, Sliwiska-Bartkowiak M, Bandosz TJ. Active pore space utilization in nanoporous carbon-based supercapacitors: Effects of conductivity and pore accessibility. *J Power Sour* 2012;220:243-52.
53. Ania CO, Seredych M, Rodriguez-Castellon E, Bandosz TJ. Visible light driven photoelectrochemical water splitting on metal free nanoporous carbon promoted by chromophoric functional groups. *Carbon* 2014;79:432-41.
54. Bandosz TJ, Rodriguez-Castellon E, Montenegro JM, Seredych M. Photoluminescence of nanoporous carbons: Opening a new application route for old materials. *Carbon* 2014;77:651-9.
55. neutrons.ornl.gov/vision

56. Jagiello J, Olivier JP. Carbon slit pore model incorporating surface energetical heterogeneity and geometrical corrugation. *Adsorption* 2013;19:777-83.
57. Moulder JF, Stickle WF, Sobol PE, Bomben, KD. *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Minneapolis, USA, 1992.
58. Mitchell PCH, Parker SF, Ramirez-Cuesta A, Tomkinson J. *Vibrational Spectroscopy with Neutrons, with applications in Chemistry, Biology, Materials Science and Catalysis. Series on Neutron Techniques and Applications, Vol. 3*, World Scientific, London, 2005.
59. Zhang S, Kang P, Ubnoske S, Brennaman MK, Song N, House RL, et al. Polyethylenimine-enhanced electrocatalytic reduction of CO₂ to formate at nitrogen-doped carbon nanomaterials. *J Am Chem Soc* 2014;136:7845-8.

Captions to the Tables

Table 1. Content of elements on the surface (in at. %).

Captions to the Figures

Fig. 1. a) Pore size distributions; b) CO₂ adsorption isotherms; c) The comparison of the CO₂ adsorption capacity measured at equilibrium at 0.01 MPa and 0.1 MPa; and d) Heat flow curves for CO₂ adsorption (the values of the integrated heats of CO₂ adsorption are included in the Figure).

Fig. 2. a) The isothermal (30 °C) CO₂ adsorption profiles and b-d) m/z thermal profiles recorded during CO₂ adsorption for the materials studied.

Fig. 3. Surface concentration the specific carbon, oxygen, nitrogen and sulfur functionalities present on the carbon surface.

Fig. 4. C 1s, O 1s, N 1s and S 2p core energy levels for the polymer-derived activated carbon (C-AO).

Fig. 5. The difference INS spectra before and after CO₂ dosing in C-AO, in comparison with the reference spectra for bulk solid CO₂ and H₂O. Signal from the background and the blank CAO has been subtracted. Inset shows the INS spectrum of the blank C-AO before dosing (note that the energy scale is different).