

# A Thermodynamic Investigation of Adsorbate-Adsorbate Interactions of Carbon Dioxide on Nanostructured Carbons

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## Abstract

A thermodynamic study of carbon dioxide adsorption on a zeolite-templated carbon (ZTC), a superactivated carbon (MSC-30) and an activated carbon (CNS-201) was carried out at temperatures from 241 to 478 K and pressures up to  $5.5 \cdot 10^6$  Pa. Excess adsorption isotherms were fitted with generalized Langmuir-type equations, allowing the isosteric heats of adsorption and adsorbed-phase heat capacities to be obtained as a function of absolute adsorption. On MSC-30, a superactivated carbon, the isosteric heat of carbon dioxide adsorption *increases* with occupancy from 19 to 21  $\text{kJ} \cdot \text{mol}^{-1}$ , before decreasing at high loading. This increase is attributed to attractive adsorbate-adsorbate intermolecular interactions as evidenced by the slope and magnitude of the increase in isosteric heat and the adsorbed-phase heat capacities. An analysis of carbon dioxide adsorption on ZTC indicates a high degree of binding-site homogeneity. A generalized Law of Corresponding States analysis indicates lower carbon dioxide adsorption than expected.

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## Introduction

Anthropogenic contributions to carbon dioxide in the atmosphere have become an ever-increasing concern, recently highlighted by the IPCC Fifth Assessment Report<sup>1</sup>. Given the growing nature of world energy demands and our continued reliance on fossil fuels, carbon-capture and storage (CCS) should be considered in any plan to mitigate climate change.<sup>2,3</sup>

Physisorptive materials are promising for a variety of gas applications because they require only low regeneration energies and are stable through thousands of cycles.<sup>4,5</sup> In physisorption, solid adsorbents induce a local densification of gas at the adsorbent surface by weak physical interactions. Physisorptive materials have been widely used for gas storage applications.<sup>6,7</sup> Because different gases adsorb to a given surface with differing selectivities, physisorptive materials are also promising for gas separations.<sup>8,9</sup> A number of studies have shown that physisorptive materials are viable candidates for separating carbon dioxide from mixed-gas streams.<sup>10,11,12</sup>

An adsorbent's selectivity of one gas over another is dependent on the thermodynamic properties of the gas-adsorbent system. As gas molecules are adsorbed, their molar entropy decreases. This is offset by a decrease in molar enthalpy from favorable interactions between the adsorbate and the adsorbent. The differential change in molar enthalpy at constant surface occupancy, defined as the isosteric enthalpy of adsorption ( $\Delta H_{ads}$ ), is an important and readily accessible figure of merit for physisorptive processes.<sup>13</sup> Optimizing the isosteric enthalpy of adsorption has been the topic of active research.<sup>14,15,16</sup> A variety of high surface area

materials including metal-organic frameworks, covalent-organic frameworks, zeolites, zeolite-templated carbons and activated carbons have been investigated as carbon dioxide adsorbents, and have exhibited isosteric heats of adsorption of up to  $90 \text{ kJ}\cdot\text{mol}^{-1}$ .<sup>17,18,19,20,21,22,23</sup>

In general the isosteric heat of adsorption ( $-\Delta H_{ads}$ ) decreases as a function of surface loading due to heterogeneity of the binding sites.<sup>24</sup> This has the effect of limiting the pressure range over which gas separation and storage are optimal. However, recent investigations of nonideal gases adsorbed on carbonaceous materials at high pressures have shown that, in some systems, strong lateral intermolecular interactions between adsorbate molecules can lead to an isosteric heat of adsorption that increases with increasing occupancy near ambient temperatures.<sup>25,26,27,28</sup> This effect is realized in adsorbent materials with optimal surface structure and a narrow distribution of binding-site energies.<sup>29,30</sup> At high pressures, carbon dioxide gas has strong intermolecular interactions and non-ideal behavior, and is therefore a candidate for this effect. In this paper we report that the superactivated carbon MSC-30 has an atypical, increasing isosteric heat of carbon dioxide adsorption, and we provide evidence that this effect derives from adsorbate-adsorbate intermolecular interactions.

## Experimental Methods

Carbon dioxide uptake was measured on three carbonaceous materials: CNS-201, MSC-30 and ZTC. The activated carbon CNS-201 was obtained from A.C. Carbons Canada Inc., and MSC-30, a superactivated carbon, was obtained from

Kansai Coke & Chemicals Company Ltd. ZTC was synthesized by infiltrating zeolite NaY with furfuryl alcohol followed by polymerization, carbonization and the ultimate dissolution of the zeolite template. This synthesis has been described in detail elsewhere.<sup>31</sup> Each material was degassed at 520 K under vacuum (less than  $10^{-3}$  Pa) prior to measurements. The skeletal densities of the materials were determined by helium pycnometry.

Equilibrium N<sub>2</sub> adsorption isotherms were measured at 77 K with a BELSORP-max volumetric instrument (BEL-Japan Inc.), and surface areas were calculated using the Brunauer-Emmett-Teller (BET) method<sup>32</sup>. The Dubinin-Radushkevich (DR) method<sup>33,34</sup> was used to calculate micropore volumes. Pore-size distributions were calculated by the non-local density functional theory (NLDFT) method<sup>35</sup> from high-resolution data collected on a Micromeritics ASAP 2020, using a carbon slit-pore model and software provided by Micromeritics.

Equilibrium carbon dioxide adsorption isotherms were measured at up to nine temperatures between 240 and 478 K using a custom Sieverts apparatus that was designed and tested for accuracy to 10<sup>7</sup> Pa.<sup>36</sup> The sample holder was submerged in an isothermal chiller bath for low temperature isotherms, or placed inside a cylindrical copper heat exchanger and wrapped with insulated fiberglass heating tape for high temperature isotherms. A proportional-integral-derivative (PID) controller was used to maintain a constant temperature during measurements; fluctuations were less than  $\pm 0.1$  K at low temperatures and no higher than  $\pm 0.4$  K at high temperatures.

The Sieverts apparatus is equipped with a digital cold cathode pressure sensor (I-MAG, Series 423) and a molecular drag pump capable of achieving a vacuum pressure of  $10^{-4}$  Pa. High-pressure measurements were made using an MKS Baratron (Model 833) pressure transducer. Temperature was measured on the wall of the manifold and on the outer wall of the sample holder using K-type thermocouples and platinum resistance thermometers. Supercritical fluid chromatography (SFC) grade carbon dioxide (99.995%) gas was obtained from Air Liquide America Corporation, and multiple adsorption/desorption isotherms were measured to ensure reversibility and reproducibility. Gas densities were determined from the REFPROP Standard Reference Database<sup>37</sup>.

## Results

### Nitrogen Adsorption and Helium Pycnometry

The pore-size distributions calculated by non-local density functional methods of CNS-201, MSC-30 and ZTC are shown in Figure 1. CNS-201 was found to have distinct, extremely narrow pore sizes of  $< 1.5$  nm in width. MSC-30, on the other hand, has a broad pore size distribution with pore widths ranging from 0.6 to  $>3$  nm. ZTC has a single dominant pore width of 1.2 nm, consistent with the inverse of the zeolite structure. The BET surface areas of MSC-30, CNS-201 and ZTC were found to be  $3244 \pm 28$ ,  $1095 \pm 8$  and  $3591 \pm 60$   $\text{m}^2 \cdot \text{g}^{-1}$ , respectively. ZTC is one of the highest specific surface area carbonaceous materials reported to date. The micropore volumes of MSC-30, CNS-201 and ZTC were determined to be 1.54, 0.45 and  $1.66$   $\text{mL} \cdot \text{g}^{-1}$ , respectively. The theoretical maximum possible carbon dioxide

adsorption ( $n_m$ ) was estimated as the product of the micropore volume and the density of liquid carbon dioxide at its triple point,<sup>30</sup> yielding estimated  $n_m$  values of 41.3, 12 and 44.5 mmol•g<sup>-1</sup> for MSC-30, CNS-201, and ZTC, respectively. MSC-30 and CNS-201 have skeletal densities of 2.1 g•mL<sup>-1</sup>, while ZTC has a lower skeletal density of 1.8 g•mL<sup>-1</sup> due to a higher hydrogen content<sup>38</sup>.

### Carbon Dioxide Adsorption

Equilibrium excess adsorption isotherms of carbon dioxide on the nanostructured carbons are shown in Figure 2. The low temperature isotherms display maxima at pressures between  $5 \cdot 10^5$ - $5 \cdot 10^6$  Pa, as expected for Gibbs excess quantities. At all measured temperatures, MSC-30 has the highest maximum excess adsorption quantities. At room temperature (298 K), the maximum excess uptakes on MSC-30, CNS-201 and ZTC were 22.7, 7.25 and 17.8 mmol•g<sup>-1</sup> respectively, corresponding to 7.00, 6.62 and 4.96 mmol•(1000 m<sup>2</sup>)<sup>-1</sup>. This correlation of BET surface area and Gibbs surface excess uptake maximum capacity is consistent with other similar materials, which have an average “Chahine’s-type rule” for carbon dioxide uptake at 298 K of  $\sim 7$  mmol•(1000 m<sup>2</sup>)<sup>-1</sup>.<sup>39</sup>

### Adsorption Data Analysis

Adsorption measurements give excess adsorption ( $n_e$ ), not absolute adsorption ( $n_a$ ).<sup>40</sup> At low pressures, excess adsorption approximates absolute adsorption. At high pressures, however, the absolute adsorption remains a monotonically increasing quantity, but excess adsorption does not. By utilizing a

fitting equation consistent with the definition of excess adsorption, measured data can be fitted beyond the maximum of excess adsorption. Our carbon dioxide excess adsorption isotherms were fitted using a generalized Langmuir equation, recently described and applied to high-pressure methane adsorption.<sup>29</sup> This fitting technique was adapted from that implemented by Mertens<sup>41</sup>.

The fitting procedure incorporates the Gibbs definition of excess adsorption, which is related to absolute adsorption as follows:

$$n_e = n_a - V_a \rho(P, T) \quad (1)$$

The gas density ( $\rho$ ) is a function of pressure ( $P$ ) and temperature ( $T$ ) and was estimated from the modified Benedict–Webb–Rubin equation of state<sup>37</sup>. The volume of the adsorption layer,  $V_a$ , is the only unknown preventing direct calculation of absolute adsorption. Here  $V_a$  is left as an independent fitting parameter. The Gibbs excess adsorption was fitted using the following generalized Langmuir equation:

$$n_e(P, T) = (n_{max} - V_{max} \rho(P, T)) \left[ \sum_i \alpha_i \frac{K_i P}{1 + K_i P} \right] \quad (2)$$

$$K_i = \frac{A_i}{\sqrt{T}} e^{-E_i/RT} \quad (3)$$

$$\sum_i \alpha_i = 1 \quad (4)$$

The independent fitting parameters are  $\alpha_i$  (weighting factors) and  $K_i$  (equilibrium constants) for the  $i$  Langmuir isotherms, the scaling factor  $n_{max}$ , and the maximum volume of the adsorption layer  $V_{max}$ . The equilibrium constants (Eq. 3) depend on the prefactors ( $A_i$ ) and energies ( $E_i$ ) of the Arrhenius-type exponentials and  $R$ , the universal gas constant. For a good balance between number of fitting parameters and goodness of fit, the number of superimposed Langmuir equations used was  $i=2$ .

The residual mean square values of the resulting fits of the adsorption data for MSC-30, CNS-201 and ZTC were 0.1, 0.07 and 0.7 (mmol•g<sup>-1</sup>)<sup>2</sup> respectively.

The best-fit parameters of carbon dioxide on MSC-30, CNS-201 and ZTC are compared to the best-fit parameters of methane<sup>25</sup>, ethane<sup>26</sup> and krypton<sup>27</sup> on the same materials (using the same fitting equation) in Table 1. In many cases, the fit parameters correlate to physical properties, and may sometimes be validated by comparison to independent estimates. For example, the adsorbent micropore volume can be determined by the Dubinin-Radushkevich method<sup>33</sup> and compared to  $V_{max}$ . Likewise the product of the adsorbent micropore volume and the liquid molar density of the adsorbate<sup>37</sup> ( $n_m$ ) provides an estimate of  $n_{max}$ . Rigorous comparisons of the fitted and independently estimated parameters are shown in Table 2.

Although more difficult to validate through independent comparison, the  $E_i$  parameters give important insight into the adsorbent-adsorbate binding energies of the  $i^{\text{th}}$  isotherm, and the prefactor  $A_i$  gives insight about the relative number of adsorption sites with energy  $E_i$ . Specifically, the product of  $\alpha_i$ , the  $i^{\text{th}}$  isotherm weighting factor, and  $A_i$  gives an overall “weight” of sites with energy  $E_i$ . For carbon dioxide, methane, ethane and krypton adsorption on MSC-30 and CNS-201, the contributions of each isotherm in the fitted superposition of isotherms are moderately well-balanced. No isotherm accounts for less than 1% of the overall “weight”, except for carbon dioxide on MSC-30. This may result from carbon dioxide adsorbing on a more limited set of MSC-30 adsorption sites than other gases, as noted on single-wall carbon nanotube bundles<sup>42</sup>.



For ZTC, each generalized Langmuir fit heavily favors just a single isotherm (see Table 3). This suggests that ZTC usually has a higher degree of binding-site homogeneity than MSC-30 or CNS-201, consistent with the pore-size distributions of the three carbonaceous adsorbents. Unlike MSC-30 and CNS-201, ZTC has a single sharply peaked pore width (1.2 nm). In microporous carbons, the predominant contribution to binding-site heterogeneity often results from the spectrum of pore widths. ZTC eliminates much of this heterogeneity with its micropores of approximately a constant width.

The Clausius-Clapeyron relation was used to determine the isosteric enthalpy of adsorption:

$$q_{st} = -\Delta H_{ads}(n_a) = -T \left( \frac{\partial P}{\partial T} \right)_{n_a} (\Delta v_{ads}) \quad (5)$$

Here the isosteric heat of adsorption ( $q_{st}$ ) is (by convention) a positive value when adsorption is exothermic. The coverage-dependent change in enthalpy upon adsorption is  $\Delta H_{ads}(n_a)$ . The change in molar volume of the adsorbate upon adsorption is  $\Delta v_{ads}$ .

## Discussion

### Isosteric Heat of Carbon Dioxide Adsorption

The isosteric heats of carbon dioxide adsorption on MSC-30, CNS-201 and ZTC derived according to Eq. 5 are shown in Figure 3. The isosteric heat of carbon dioxide adsorption on MSC-30 differs significantly from that on a conventional activated carbon like CNS-201 in its dependence on absolute uptake. For carbon

dioxide adsorption on CNS-201, the isosteric heat displays typical behavior. It is a decreasing function of occupancy. On the other hand, the isosteric heat of carbon dioxide adsorption on MSC-30 first increases as a function of occupancy before reaching a maximum, and then decreases at high occupancy. On ZTC, the isosteric heat of carbon dioxide adsorption decreases very gradually with loading, especially at low temperatures where the slope is  $\sim -25 \text{ kJ}\cdot\text{mol}^{-2}$ . This behavior is in agreement with the high degree of binding-site homogeneity expected from the pore-size distribution and fit parameters for ZTC. Carbon dioxide adsorption differs from methane, ethane and krypton adsorption where the isosteric heats on MSC-30 decrease with occupancy, while the isosteric heats on ZTC increase with occupancy due to enhanced adsorbate-adsorbate interactions. This suggests that carbon dioxide adsorbate-adsorbate interactions are better optimized for the micropore distribution of MSC-30 than ZTC.

For carbon dioxide adsorbed on MSC-30, the total increase in isosteric heat (peak value minus low coverage value) is more pronounced at lower temperatures, reaching a maximum measured increase of  $2.1 \text{ kJ}\cdot\text{mol}^{-1}$  at 241 K. This energy is consistent with lateral intermolecular interactions between adsorbed carbon dioxide molecules. For example, the well depth of the Lennard-Jones potential between two carbon dioxide molecules is  $\varepsilon = 1.8 \text{ kJ}\cdot\text{mol}^{-1}$ <sup>43</sup>.

At low temperatures and low occupancy, the isosteric heat of adsorption of carbon dioxide on MSC-30 increases approximately linearly with occupancy. This linear increase is nearly identical for the lowest temperatures measured (e.g.  $107 \text{ kJ}\cdot\text{g}\cdot\text{mol}^{-2}$  at 241 K,  $111 \text{ kJ}\cdot\text{g}\cdot\text{mol}^{-2}$  at 247 K,  $113 \text{ kJ}\cdot\text{g}\cdot\text{mol}^{-2}$  at 262 K and  $106$

kJ•g•mol<sup>-2</sup> at 283 K). Similar trends hold true for methane, ethane and krypton adsorption on ZTC.<sup>25,26,27</sup> The gases with stronger intermolecular interactions have larger slopes, consistent with the hypothesis that the increases in the isosteric heats with loading result from adsorbate-adsorbate intermolecular interactions. The slopes of the isosteric heats with respect to fractional occupancy,  $\frac{\partial(-\Delta H_{ads})}{\partial\theta}$ , may be reasonably estimated with Eq. 6 (see Table 4) in the low coverage regime

$$\frac{\partial(-\Delta H_{ads})}{\partial\theta} = \frac{z\varepsilon}{2} \quad (6)$$

where the coordination number,  $z$ , is posited to be 5 and  $\varepsilon$  is the well depth of the Lennard-Jones 12-6 interaction potential<sup>43</sup>. This simple first approximation (Eq. 6) assumes that adsorbed molecules are randomly situated and only interact with first nearest neighbors, each interaction having strength  $\varepsilon$ .

A qualitatively similar increase in the isosteric heat of carbon dioxide adsorption on Maxsorb<sup>®</sup> (from Kansai Netsu Kagaku Co.) was previously noted by Himeno et al.<sup>44</sup>, however it is unclear to what degree those results are quantitatively accurate. Himeno et al. use the Toth equation to analyze three experimental isotherms, making a number of simplifying assumptions in the process (e.g., assuming the validity of the ideal gas law, assuming that absolute adsorption equals excess adsorption, assuming the isosteric heat has no temperature dependence, and assuming a zero-volume adsorbed phase). Many of these assumptions break down under the high-pressure conditions tested in this work. We employ a generalized Langmuir-type fitting function that determines absolute adsorption and gives

isosteric, not isoexcess, heats of adsorption.<sup>25</sup> We have elaborated on this methodology in detail in prior publications and found that eliminating idealized assumptions contributes significantly to the accuracy of the results.<sup>25,29</sup> Himeno et al. report an increasing isosteric heat for carbon dioxide adsorption on Maxsorb® with a slope of  $\sim 300$  ( $\text{kJ}\cdot\text{g}\cdot\text{mol}^{-2}$ ). We report a more moderate slope ( $\sim 110$   $\text{kJ}\cdot\text{g}\cdot\text{mol}^{-2}$ ) on the comparable superactivated carbon MSC-30 after considering isotherms taken at eight temperatures. This more moderate increase is more consistent with the strength of carbon dioxide intermolecular interactions as measured by the Lennard-Jones parameter,  $\epsilon=1.8$   $\text{kJ}\cdot\text{mol}^{-1}$ <sup>43</sup>, Eq. 6 and the trend in Table 3.

### **Adsorbed-Phase Enthalpies and Heat Capacities**

The adsorbed-phase enthalpies for carbon dioxide adsorption on MSC-30, CNS-201 and ZTC were calculated as a function of absolute adsorption by subtracting the isosteric heats in Figure 3 from gas phase enthalpy values determined from data tables at equivalent conditions<sup>37</sup>. Figure 4 shows that MSC-30 has different behavior than CNS-201 or ZTC in that the adsorbed-phase enthalpy is not a monotonically increasing function of coverage. Rather the adsorbed-phase enthalpy on MSC-30 decreases with coverage at low temperatures and low coverages, consistent with enhanced favorable adsorbate-adsorbate interactions.

The adsorbed-phase constant pressure heat capacities of carbon dioxide on MSC-30, CNS-201 and ZTC were calculated by taking the partial derivative of the

adsorbed-phase enthalpies with respect to temperature at constant pressure. Figure 5 shows the adsorbed-phase heat capacities at a constant sample pressure of  $2 \cdot 10^6$  Pa.

Figure 5 shows that the constant pressure adsorbed-phase heat capacities of carbon dioxide on CNS-201 and ZTC gradually increase with temperature as expected for a polyatomic gas. The adsorbed-phase heat capacity on ZTC is within 15% of the gas-phase heat capacity at the same temperature and pressure conditions, except at temperatures below 264K where carbon dioxide approaches the liquid phase. On CNS-201, the adsorbed-phase heat capacity has similar qualitative trends, but with more scatter in the data. On MSC-30 a different behavior is observed where the adsorbed-phase heat capacity rises significantly to a value in excess of  $100 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$  at a temperature of  $\sim 250\text{K}$ . This heat capacity is larger than the heat capacity of liquid carbon dioxide ( $\sim 94 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ )<sup>37</sup> and is suggestive of a phase transition. This suggests that the origin of the enhanced adsorbate-adsorbate interactions may be an adsorbed-phase clustering transition as previously noted in other systems.<sup>29,30</sup> Once again this suggests that cooperative carbon dioxide adsorbate-adsorbate interactions are better optimized for the micropore distribution of MSC-30 than ZTC or CNS-201. Moreover, at high temperatures, above a presumed critical temperature, the adsorbed-phase heat capacity on MSC-30 converges with the adsorbed-phase heat capacities on ZTC, CNS-201 and the corresponding gas-phase heat capacity of carbon dioxide.

## Law of Corresponding States and Selectivities

It is well established that different nonideal gases behave similarly at corresponding conditions, with equal reduced temperatures and reduced pressures.<sup>45</sup> The reduced temperature and reduced pressure are defined as the ratios of the system temperature to the gas critical temperature, and the system pressure to the gas critical pressure, respectively. We have recently reported an extension to the Law of Corresponding States that applies to physisorbed molecules.<sup>30</sup> Specifically:

*Classical gases adsorb to the same fractional occupancy on the same adsorbent at corresponding conditions.*

Fractional occupancy ( $\theta$ ) is defined as the ratio of the absolute adsorption ( $n_a$ ) to maximum possible adsorption ( $n_m$ ). To facilitate comparisons in this work and others,<sup>30</sup> we instead compare the more accessible quantity, excess occupancy ( $\theta_e$ ), defined as the ratio of excess adsorption ( $n_e$ ) to maximum possible adsorption ( $n_m$ ). For each adsorbent,  $n_m$  was estimated by multiplying the adsorbent micropore volume by the liquid molar density of the adsorbate at its triple point.<sup>30,37</sup> Carbon dioxide, ethane, methane and krypton excess occupancy isotherms on ZTC and MSC-30 are compared at corresponding conditions in Figure 6.

At low temperatures, there is reasonable agreement between carbon dioxide and ethane isotherms at corresponding conditions. At higher temperatures, however, the carbon dioxide isotherms are significantly smaller than corresponding isotherms of the other gases. This may be due in part to the large quadrupole moment of carbon dioxide<sup>46</sup>, which is not present in the other gases considered. The

large quadrupole moment accounts for ~50% of the cohesive energy of solid carbon dioxide.<sup>47,48</sup> Notably the bulk critical temperature and isosteric heats of carbon dioxide and ethane are similar in spite of carbon dioxide's significantly lower polarizability. This is also consistent with a strong quadrupole interaction of carbon dioxide.<sup>49,50,51</sup> It is possible that the short-range quadrupole-induced dipole interactions between carbon dioxide and the adsorbent are disrupted with temperature, but further investigation is needed.

The selectivities of carbon dioxide with respect to methane, ethane and krypton were calculated as the ratio of the Henry's Law constants. Henry's Law constants were calculated directly from the excess adsorption data by extrapolating to zero coverage the logarithm of pressure divided by excess adsorption ( $\ln(P/n_e)$ ).<sup>52</sup> The measured room temperature Henry's Law constants and selectivities are given in Table 5. Methane and krypton have similar Henry's Law constants, as one might expect based on the similarity of the gases, particularly their similar critical temperatures. While carbon dioxide and ethane have nearly identical critical temperatures, ethane has significantly higher room temperature Henry's Law constants for each adsorbent. This is consistent with the trends noted in Figure

6.

## Conclusions

The excess uptakes of carbon dioxide on MSC-30, CNS-201 and ZTC were measured volumetrically and fitted with a generalized Langmuir-type equation. The fitted data were used in thermodynamic analyses that show how MSC-30 exhibits an atypical, increasing isosteric heat of carbon dioxide adsorption, while CNS-201 has the thermodynamic properties of a conventional carbon. The isosteric heat on ZTC suggests a high degree of binding-site homogeneity. At near-ambient temperatures the isosteric heat on MSC-30 rises with uptake from 19 to 21 kJ•mol<sup>-1</sup>. The measured adsorbed-phase enthalpies, adsorbed-phase heat capacities, and comparisons to studies with other nonideal gases indicate that this increasing isosteric heat results from enhanced adsorbate-adsorbate interactions within the pores of MSC-30.

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**List of Figure Captions:**

Figure 1. The pore-size distribution of MSC-30, CNS-201 and ZTC as calculated by the NLDFT method.

Figure 2. Equilibrium excess adsorption isotherms of carbon dioxide on MSC-30 (top), ZTC (middle) and CNS-201 (bottom). The curves show the best simultaneous fit of the measured data for a given material, using Equation 2 below.

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Figure 6. Comparison of carbon dioxide (+), ethane ( $\Delta$ ), methane (■) and krypton (•) excess occupancies at corresponding conditions (with reduced temperatures given in the key).

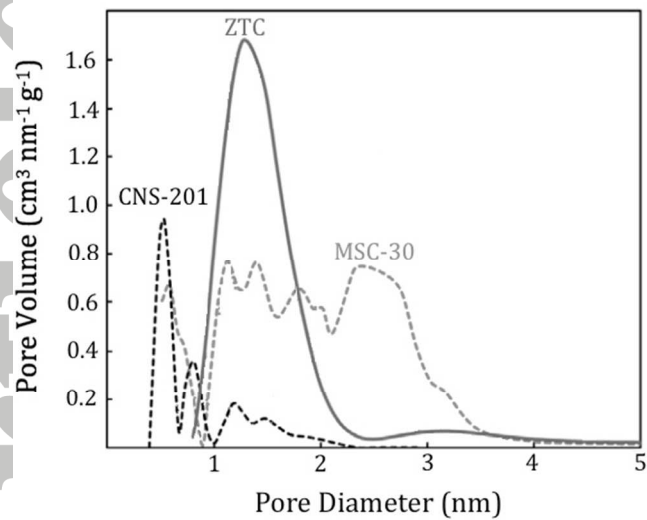


Figure 1. The pore-size distribution of MSC-30, CNS-201 and ZTC as calculated by the NLDFT method.



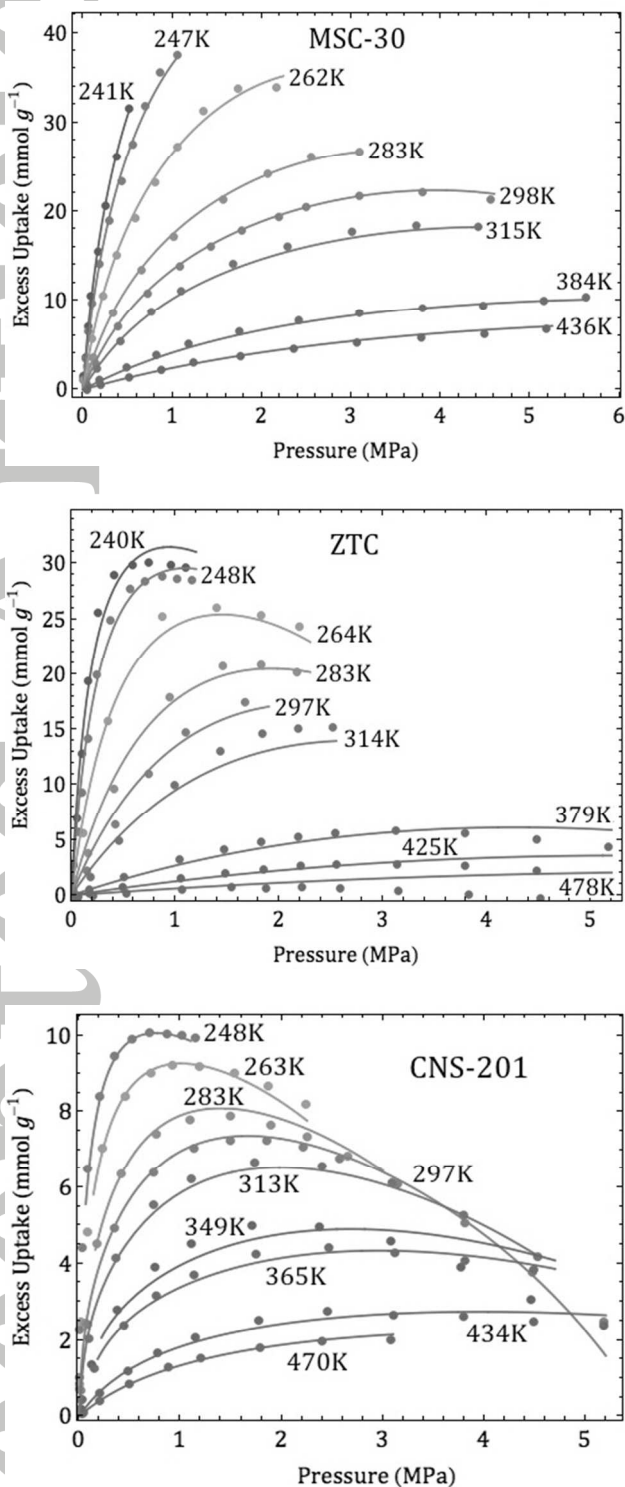


Figure 2. Equilibrium excess adsorption isotherms of carbon dioxide on MSC-30 (top), ZTC (middle) and CNS-201 (bottom). The curves show the best simultaneous fit of the measured data for a given material, using Equation 2 below.

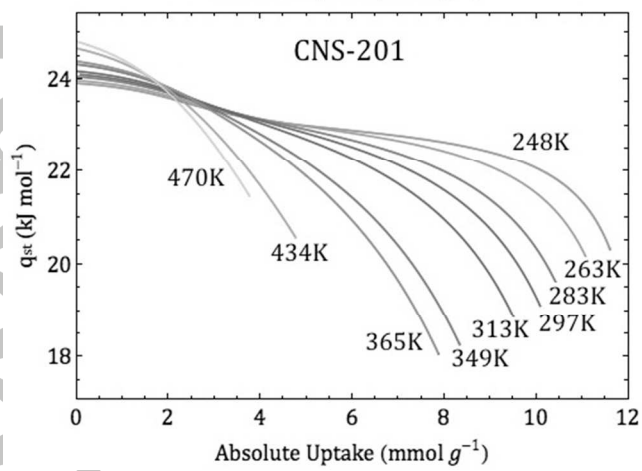
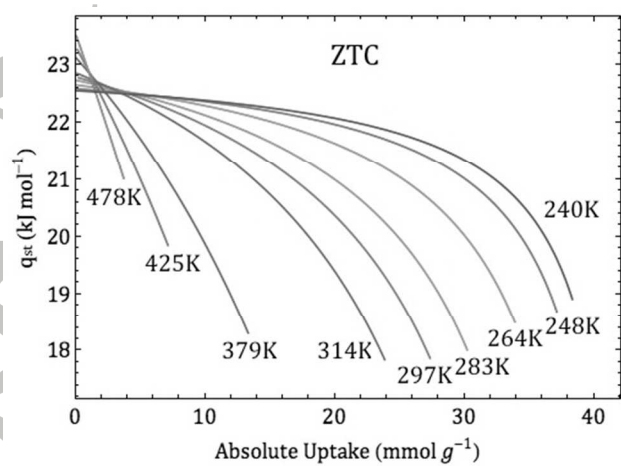
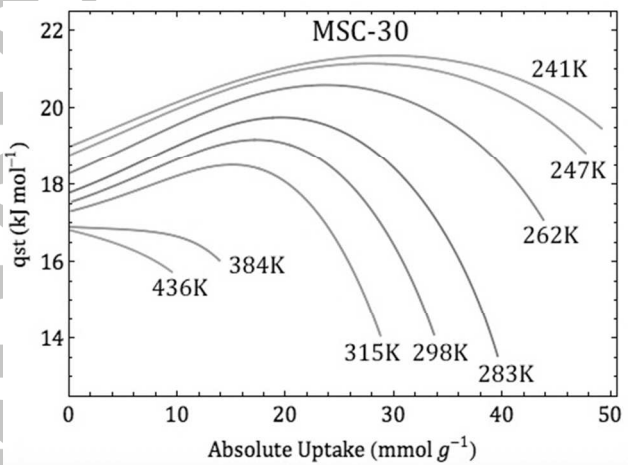


Figure 3. Isosteric heats of adsorption of carbon dioxide on CNS-201, MSC-30 and ZTC as a function of absolute uptake.

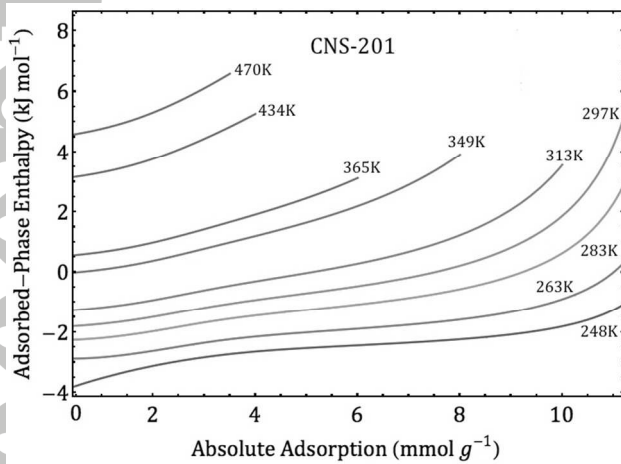
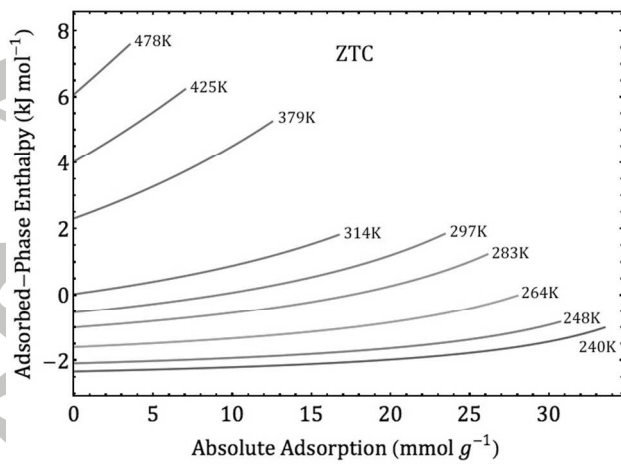
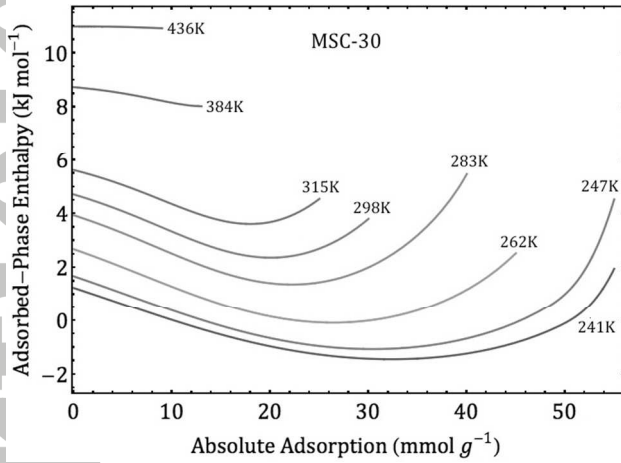


Figure 4. Adsorbed-phase enthalpies of carbon dioxide on MSC-30, ZTC and CNS-201.

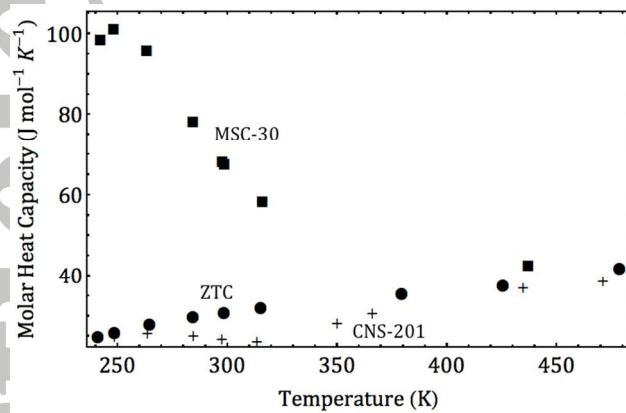


Figure 5. Adsorbed-phase molar heat capacities of carbon dioxide on MSC-30 (■), CNS-201 (+) and ZTC (●). Values are given at a constant sample pressure of 2 MPa.

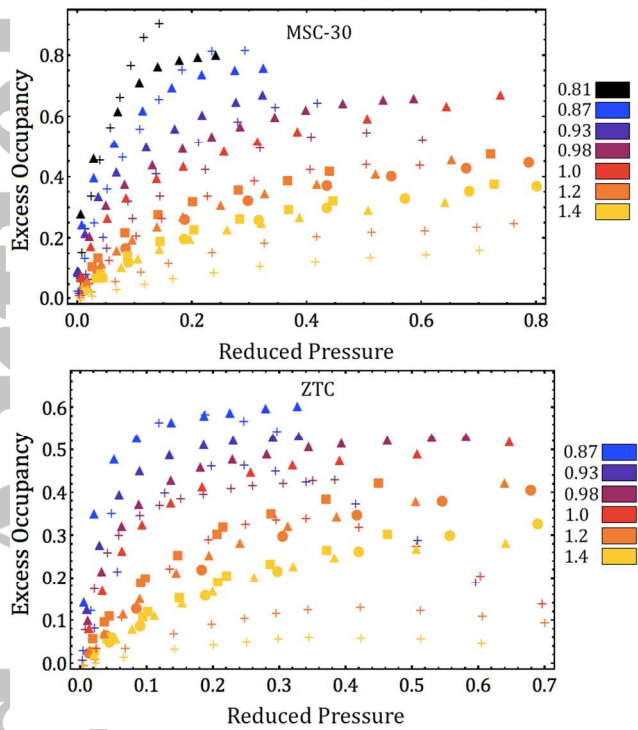
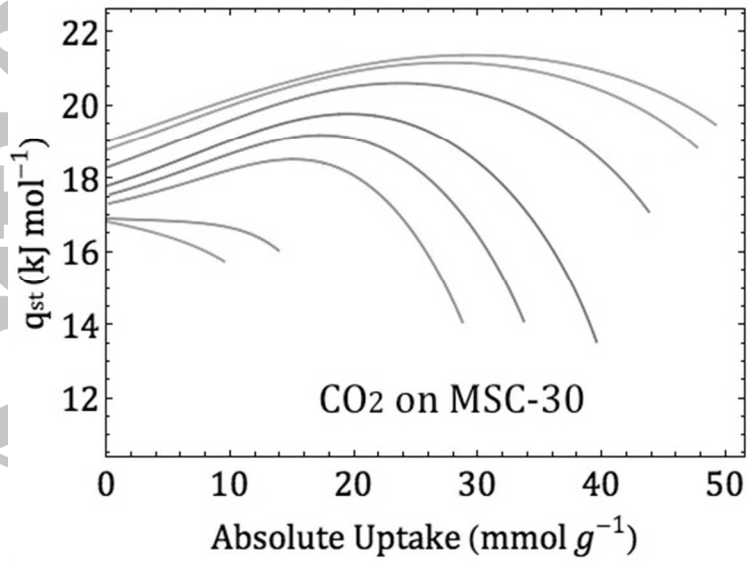


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“TOC Graphic”



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**Table 1. Best-fit parameters from Generalized Langmuir Fits.**

	$n_{max}$ (mmol g <sup>-1</sup> )	$\alpha$	$V_{max}$ (mL g <sup>-1</sup> )	$A_1$ (k <sup>1/2</sup> MPa <sup>-1</sup> )	$E_1$ (kJ mol <sup>-1</sup> )	$A_2$ (k <sup>1/2</sup> MPa <sup>-1</sup> )	$E_2$ (kJ mol <sup>-1</sup> )
CO <sub>2</sub> /ZTC	45.4	1.64E-12	12.4	0.00143	21.6	0.121	3.94
CO <sub>2</sub> /CNS-201	12.9	0.800	3.41	0.0456	23.0	0.00244	22.0
CO <sub>2</sub> /MSC-30	81.1	0.207	10.0	0.000107	23.6	0.0635	14.3
CH <sub>4</sub> /ZTC	35.6	0.460	2.04	0.0590	11.6	0.000180	20.4
CH <sub>4</sub> /CNS-201	9.77	0.580	0.490	0.0610	17.2	0.00440	16.4
CH <sub>4</sub> /MSC-30	41.0	0.700	2.30	0.0680	13.4	0.00460	12.9
C <sub>2</sub> H <sub>6</sub> /ZTC	25.0	0.827	1.58	2.14E-07	41.0	0.0444	18.5
C <sub>2</sub> H <sub>6</sub> /MSC-30	36.1	0.713	2.60	0.0865	19.8	0.00647	17.8
Kr/ZTC	39.3	0.686	2.02	1.81E-06	30	0.0924	10.0
Kr/CNS-201	10.9	0.462	0.490	0.00590	15.1	0.0689	16.3
Kr/MSC-30	57.8	0.726	2.98	0.112	11.6	0.00306	12.8

**Table 2. Comparison of  $V_{max}$  and  $n_{max}$  Parameters to Independent Estimates**

	$V_{max}$ (mL g <sup>-1</sup> )	micropore volume (mL g <sup>-1</sup> )	$n_{max}$ (mmol g <sup>-1</sup> )	$n_m$ (mmol g <sup>-1</sup> )
CO <sub>2</sub> /ZTC	12.4	1.66	45.4	44.5
CO <sub>2</sub> /CNS-201	3.41	0.45	12.9	12
CO <sub>2</sub> /MSC-30	10.0	1.54	81.1	41.3
CH <sub>4</sub> /ZTC	2.04	1.66	35.6	46.6
CH <sub>4</sub> /CNS-201	0.490	0.45	9.77	13
CH <sub>4</sub> /MSC-30	2.30	1.54	41.0	43.3
C <sub>2</sub> H <sub>6</sub> /ZTC	1.58	1.66	25.0	36.0
C <sub>2</sub> H <sub>6</sub> /MSC-30	2.60	1.54	36.1	33.4
Kr/ZTC	2.02	1.66	39.3	48.5
Kr/CNS-201	0.490	0.45	10.9	13
Kr/MSC-30	2.98	1.54	57.8	45.0



**Table 3. Normalized Relative Weights of Isotherms 1 and 2 as Determined by Multiplying the Isotherm Weighting Value ( $\alpha_i$ ) by the Isotherm Prefactor ( $A_i$ )**

	Isotherm 1 Weight	Isotherm 2 Weight
CO <sub>2</sub> /ZTC	1.94E-14	1.00E+00
CO <sub>2</sub> /CNS-201	9.87E-01	1.32E-02
CO <sub>2</sub> /MSC-30	4.40E-04	1.00E+00
CH <sub>4</sub> /ZTC	9.96E-01	3.57E-03
CH <sub>4</sub> /CNS-201	9.50E-01	4.96E-02
CH <sub>4</sub> /MSC-30	9.72E-01	2.82E-02
C <sub>2</sub> H <sub>6</sub> /ZTC	2.30E-05	1.00E+00
C <sub>2</sub> H <sub>6</sub> /MSC-30	9.71E-01	2.92E-02
Kr/ZTC	4.28E-05	1.00E+00
Kr/CNS-201	6.85E-02	9.32E-01
Kr/MSC-30	9.90E-01	1.02E-02

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**Table 4. Measured and Estimated Slopes of Increasing Isothermic Heats for Methane, Ethane and Krypton on ZTC and Carbon Dioxide on MSC-30 as a Function of Fractional Occupancy (at Low Coverage and Low Temperature)**

	Estimated Slope (kJ•mol <sup>-1</sup> )	Measured Slope (kJ•mol <sup>-1</sup> )
Methane	3.0	3.2
Krypton	3.3	3.4
Ethane	4.3	4.0
Carbon Dioxide	4.5	4.5

**Table 5. Henry's Law Constants ( $\text{mmol}\cdot\text{g}^{-1}\text{MPa}^{-1}$ ) and Equilibrium Adsorption Selectivities at Room Temperature**

Henry's Law Constants	ZTC	MSC-30	CNS-201
C <sub>2</sub> H <sub>6</sub>	45.7	51.9	35.1
CO <sub>2</sub>	19.7	19.9	21.4
CH <sub>4</sub>	7.03	8.99	6.99
Kr	6.80	9.03	6.57
CO <sub>2</sub> /CH <sub>4</sub>	2.80	2.21	3.06
C <sub>2</sub> H <sub>6</sub> /CO <sub>2</sub>	2.32	2.61	1.64
CO <sub>2</sub> /Kr	2.90	2.20	3.26
C <sub>2</sub> H <sub>6</sub> /CH <sub>4</sub>	6.50	5.77	5.02
C <sub>2</sub> H <sub>6</sub> /Kr	6.72	5.75	5.34