Microcalorimetric Study of the Influence of Surface Chemistry on the Adsorption of Water by High Surface Area Carbons

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Microcalorimetric techniques have been employed to investigate the adsorption of water on chemically modified, high surface area carbons. A matrix of treatments and carbons were selected to test some hypotheses. Heats of adsorption of water indicate that adsorption is a strong function of surface chemistry. Three mechanisms of water adsorption are delineated according to measured differential heats of adsorption (H_{ads}): (i) chemical adsorption with $H_{ads} > 12$ kcal/mol, (ii) condensation with H_{ads} approximately 10 kcal/mol, and (iii) physical adsorption with $H_{ads} < 10$ kcal/mol. The absolute and relative amounts of water adsorption arising from each mechanism are a function of surface chemistry. Adsorption of water on carbons dried at 175 °C in N_2 generates typical Type V adsorption isotherms. Heat of adsorption data for water adsorbed on dried carbon indicates that condensation accounts for the sharp rise in adsorption at a relative humidity of approximately 0.5. Treating carbons with N_2 at 950 °C generates surfaces that initially adsorb water through a mechanism of chemical adsorption, followed by condensation, and finally physical adsorption. On high-temperature N_2-treated carbons heats of adsorption exceed 100 kcal/mol, suggesting chemisorption of water at unsaturated carbon surface sites produced during the high-temperature reduction of oxygen species. Carbons reduced with H_2 at 950 °C are hydrophobic, and microcalorimetric data reveals that the small amount of adsorption observed arises from either chemical or physical adsorption rather than condensation. Hydrophobic carbon surfaces subsequently oxygenated at 150 °C showed significant increases in the amount of water adsorbed through physical adsorption. These results demonstrate that microcalorimetric techniques complement standard isotherm measurements in describing the nature of water adsorption on carbon surfaces.

Introduction

The adsorption of water at solid surfaces is of compelling scientific and engineering interest for a number of reasons. Scientific interest stems from the unusual nature of water adsorption process (**1**−**7**). The dynamics of water adsorption at surfaces, driven in large part by hydrogen bonding interactions, are richly varied compared with adsorption studies of nonassociating molecules. Water adsorption dynamics are strongly dependent on the presence and geometrical arrangement of surface chemical functionalities, for instance, adsorbed O, OH, P, Cl, and unsaturated carbon sites, that can act as nucleation sites, or primary adsorption sites, initiating the formation of adsorbed water clusters (**3, 8**−**10**). Engineering interest is directed at understanding the role of surface chemistry in controlling water adsorption on carbon surfaces. Such understanding may lead to improved strategies for creating selective carbon adsorbers in applications such as corrosion prevention and environmental remediation. Indeed, there has been a marked increase in the use of carbon adsorbers to remove pollutants from exhaust gas streams that invariably contain water (**11**). Recent reports indicate that hydrophilic carbons do not function well for these applications, as water molecules block active sites. These findings suggest a need to generate hydrophobic surfaces for unique applications. Recent studies indicate that surface chemistry can dramatically impact adsorption selectivity from the gas phase. For example, the selectivity of surfaces for NO_x adsorption (rather than O_2 adsorption) can be controlled (**12**). The distribution of acid sites on a carbon surface also depends on carbon pretreatment chemistry (**13**).

We recently demonstrated that the adsorption of oxygen and concomitant generation of acid sites on high surface area carbons is influenced by gas treatments that dictate the surface chemistry of the carbon (**12**−**16**). In particular, it was demonstrated that reduction of the carbons with H_2 or N_2 at 900 °C produces surfaces with unique chemistries. While both high-temperature H_2 and N_2 treatments generate oxygen free, basic carbon surfaces, N_2 treated surfaces contain highly unsaturated carbon atoms that rapidly re-adsorb oxygen, leading to rapid re-acidification of the surface. The H_2 treated carbon, in contrast, retains a basic surface and does not adsorb oxygen even after several months of exposure to ambient conditions.

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Water adsorption is a useful probe to further study the influence of modifications in carbon surface chemistry for a number of reasons. First, the validity of experimental techniques can be verified by comparison to adsorption isotherms published for water adsorption on standard materials. Second, despite extensive experimental and theoretical studies, the mechanism of water adsorption and the role of surface chemistry on the adsorption process are still a matter of debate. For example, experimental observations of water adsorption, and associated models developed to explain these observations, indicate that high-energy primary adsorption sites (PAS) initiate water cluster formation and induce condensation (**3, 17−21**). Here, PAS is taken to be, as suggested by others (**2**), a site on the carbon framework that promotes water adsorption through specific interactions between the water molecule and carbon surface. This definition of PAS defines the adsorption interaction on a molecular level, and includes both islanding and monolayer adsorption mechanisms. However, the adsorption of water is still often theoretically modeled by assuming a layer-by-layer mechanism implying condensation (**7, 22**). For water adsorption on hydrophobic carbon and silica surfaces, isosteric heats of adsorption are generally measured to be lower than the heat of condensation (**8−10, 23**), indicating relatively weak water-surface interactions and a noncondensation adsorption mechanism.

We delineate here the mechanism of water adsorption on high surface area carbons using measurements of adsorption isotherms and microcalorimetric differential heats of adsorption, H_{ads}. Our results show that surface chemistry plays a substantial role in dictating the adsorption mechanism of water on carbon surfaces. Adsorption of water on carbons treated with N_2 at 950 °C occurs through chemical adsorption, condensation, and physical adsorption. Hydrophobic carbon surfaces, resulting from H_2 treatment at 950 °C, adsorb small amounts of water, primarily by physical adsorption. Oxidizing hydrophobic carbons enhances greatly their ability to adsorb water through physical adsorption.

These studies indicate the usefulness of calorimetric measurements in describing the varied mechanisms of water adsorption on chemically modified carbon surfaces. Microcalorimetric techniques provide direct evidence of the physical adsorption of water on carbon surfaces at pressures where adsorption isotherms cannot reliably distinguish between physical adsorption and condensation. The present study complements previous work regarding the adsorption of water on hydrophobic surfaces (**8−10, 23**), in which H_{ads} and IR spectroscopy indicated weak carbon−water interactions arising from the physical adsorption of water.

Experimental Details

Two commercial activated carbons were employed in the experiments described below. Norit-C granular, a high purity carbon prepared from a wood precursor by phosphoric acid activation, has a BET surface area of 1378 m^2/g and a nominal pore diameter of 2−3 nm. Samples of Norit-C were ground to approximately 1 mm diameter prior to use. BPL, from Calgon Carbon Corporation was used without grinding (approximately 3 mm diameter particle size and 2 nm nominal pore diameter). We note that particle size and porosity distributions are not changed with pretreatment methods used here.

A Calvet-style microcalorimeter, described in detail elsewhere (**24**), was used in the adsorption studies. The system was modified for studies of water adsorption. Specifically, a Pyrex vessel containing deionized, degassed, and doubly distilled water was placed outside the microcalorimeter oven and attached to the dosing volume using stainless steel tubing. The vessel and tubing were wrapped with heating tape and held at a temperature below 60 °C. The water in the Pyrex vessel was maintained at a temperature 10 °C lower than the microcalorimeter to prevent condensation within the microcalorimeter.

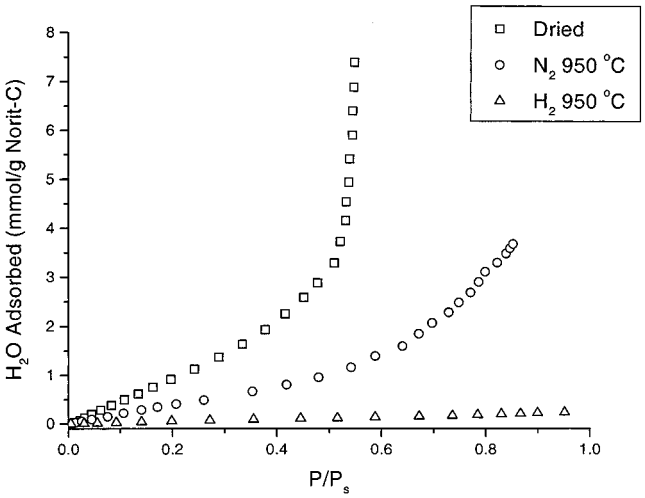

Figure 1. Water adsorption isotherms taken at 70 °C, on Norit-C carbon dried at 175 °C, N_2 treated at 950 °C, and H_2 treated at 950 °C.

The microcalorimeter allows for samples to be pretreated under controlled temperatures and gas environments and then gravity transferred to the sample cell without exposure to air. After transfer, samples were held in the microcalorimeter for 20 h at 70 °C and 10^{-5} Torr.

Calibrated exposures of H_2O from the Pyrex vessel were introduced into the sample cell sequentially as is conventionally done. The number of moles of water contained in the gas phase was computed on the basis of molar volumes tabulated in standard steam tables. Adsorption isotherms and differential heats of adsorption were extracted using this procedure. Water adsorption isotherms were plotted as water uptake versus normalized equilibrium pressure, P/P_s, where P_s is the saturation pressure of water at the temperature of the microcalorimeter (70 °C). Each microdose exposure and adsorption of water generates heat that is measured by thermopiles surrounding the sample cell. Computer recorded heat signal ballistic curves were integrated and divided by the amount of gas adsorbed to yield differential heats of adsorption. Heat of adsorption data is plotted as a function of moles of water adsorbed. Data collection in each case was terminated after approximately 25 sequential water doses, corresponding to a 48 h collection period, as the fundamental nature of the process was clear.

Results

Shown in Figure 1 are water adsorption isotherms for Norit-C dried at 175 °C, H_2 treated at 950 °C, and N_2 treated at 950 °C. Pretreatment conditions dramatically influence water adsorption on this carbon surface. First, dried Norit-C adsorbs the largest amount of water, greater than 7 mmol of H_2O/g of carbon at P/P_s of approximately 0.5. Nitrogen treated Norit-C adsorbs only 4 mmol of H_2O/g of carbon at P/P_s of 0.85, while H_2 treated Norit-C adsorbs only approximately 0.2 mmol of H_2O/g of Norit-C even near saturation pressure. Second, the shape of the

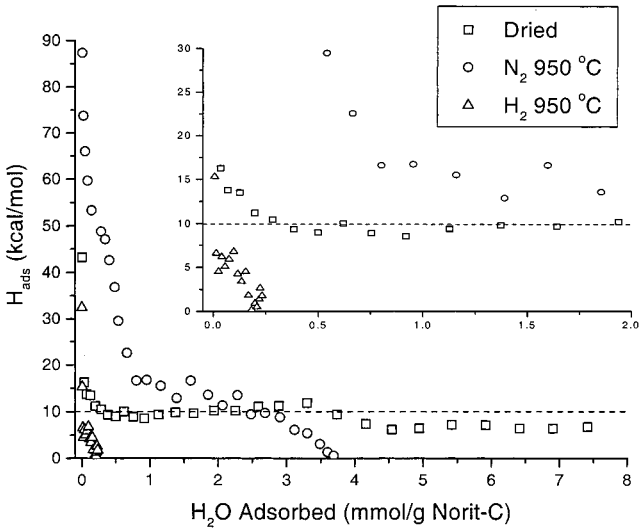

Figure 2. Heats of adsorption for water as a function of amount adsorbed on Norit-C carbon samples shown in Figure 1. The horizontal dashed line corresponds to the heat of condensation, and error bars are approximately given by the size of the symbols.

adsorption isotherm is dependent on sample pretreatment. On the H_2 treated Norit-C, the small amount of water adsorption is linear with P/P_s to high relative pressure. However, on dried and N_2 treated Norit-C water adsorption increases significantly with P/P_s after threshold relative pressures of 0.5 P/P_s and 0.6 P/P_s, respectively, are reached. The dramatic increase in the amount of water adsorbed above the threshold P/P_s is more significant for dried Norit-C than for N_2 treated Norit-C.

Shown in Figure 2 are microcalorimetric measurements of the heat of adsorption, H_{ads}, as a function of amount of water adsorbed on Norit-C dried at 175 °C, H_2 treated at 950 °C, and N_2 treated at 950 °C. The heat of adsorption is dependent on both the amount of water adsorbed as well as sample pretreatment conditions. The majority of water that adsorbs on dried Norit-C does so with H_{ads} of approximately 10 kcal/mol, the heat of condensation of water. The heat of adsorption for water on N_2 treated Norit-C is initially almost 90 kcal/mol, but decreases quickly with further adsorption and plateaus at approximately 10 kcal/mol for adsorption of 1 to 3 mmol of H_2O/g of carbon. The heat of adsorption upon further water adsorption decreases to 6 kcal/mol and less. The amount of water adsorbed with a heat of condensation is less on the nitrogen treated Norit-C than on dried Norit-C. Note also that H_{ads} values corresponding to the largest amounts of water adsorbed on both dried and N_2 treated Norit-C are lower than the heat of condensation.

The heats of adsorption for water adsorbed on Norit-C treated with H_2 at 950 °C show a surprising feature, namely, that no water adsorbs on this surface with the heat of condensation. Initial heats of adsorption are greater than 30 kcal/mol, but decrease with additional water adsorption to below the heat of condensation. The majority of water, albeit a small total amount, that adsorbs on H_2 treated Norit-C does so with H_{ads} of 1 to 7 kcal/mol.

Further experiments were conducted to determine the influence of preadsorbed oxygen on the adsorption of water on H_2 and N_2 treated Norit-C. As shown in previous studies (**14**−**16**), treating Norit-C with H_2 or N_2 at 950 °C removes adsorbed oxygen, leaving a surface with no acid sites. Shown in Figure 3 are adsorption isotherms for H_2 and N_2 treated Norit-C, before and after subsequent surface oxygenation achieved by flowing O_2 over the samples at 150 °C for 3 h. For brevity, previously

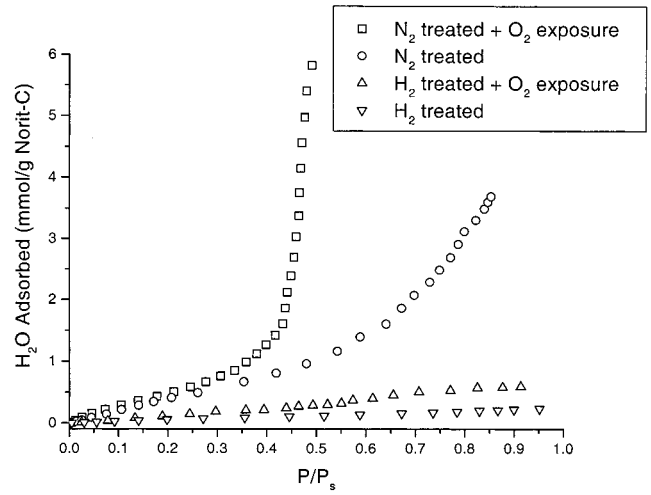

Figure 3. Water adsorption isotherms for H_2 and N_2 treated Norit-C before and after exposure to O_2.

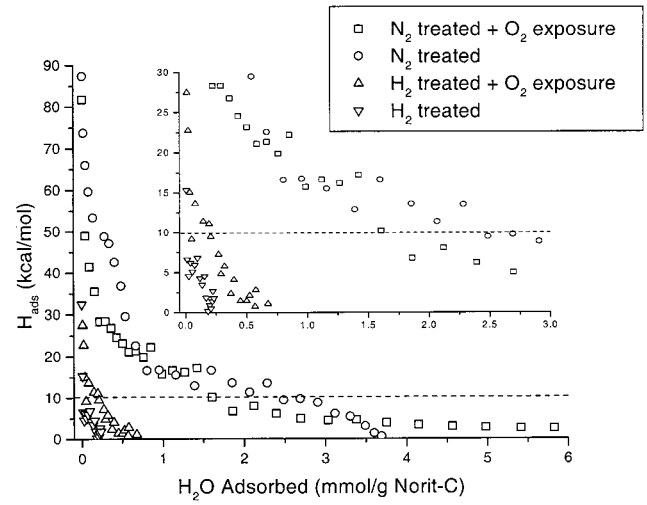

Figure 4. Heats of adsorption for water as a function of amount adsorbed for the Norit-C samples shown in Figure 3. The horizontal dashed line corresponds to the heat of condensation, and error bars are approximately given by the size of the symbols.

published adsorption isotherms for oxygen adsorption on H_2 and N_2 treated Norit-C (**14**−**16, 25**−**27**) are not repeated here. Clearly, re-acidification of the surface by the adsorption of oxygen increases the capacity of the carbon to adsorb water. Increases in oxygen acid sites result in increases in the amount of water adsorbed on both H_2 and N_2 treated Norit-C. Further, in the case of N_2 treated Norit-C, oxygenation decreases the threshold pressure for rapid increases in water condensation from P/P_s of 0.6 to 0.35. Oxygen preadsorption increases the capacity for water adsorption on N_2 and H_2 treated Norit-C surfaces by approximately one-third and a factor of 3, respectively.

Shown in Figure 4 are microcalorimetric H_{ads} measurements of water adsorbing on H_2 and N_2 treated Norit-C, before and after oxygenation. Oxygenation of N_2 treated Norit-C results in a decrease in the initial H_{ads} from almost 90 kcal/mol to less than 40 kcal/mol. However, as observed for N_2 treated Norit-C not exposed to O_2, H_{ads} decreases with further adsorption and plateaus at the heat of condensation for 1 to 3 mmol of H_2O/g of carbon. With further water adsorption H_{ads} drops below the heat of condensation. Note that additional water (corresponding to greater than 4 mmol of H_2O/g of Norit-C) adsorbs with H_{ads} below the heat of condensation, consistent with the postulate that physical adsorption dominates with increasing adsorption.

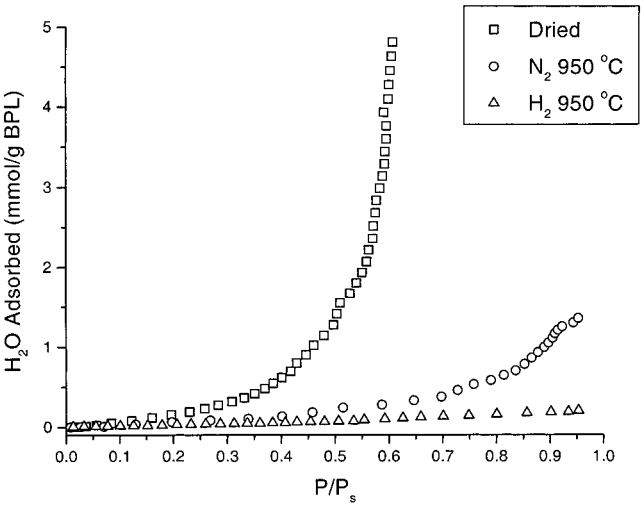

Figure 5. Water adsorption isotherms taken at 70 °C, on BPL carbon dried at 175 °C, N_2 treated at 950 °C, and H_2 treated at 950 °C.

Exposure of H_2 treated Norit-C to O_2 causes a decrease in the initial H_{ads} of water from 32 kcal/mol to 28 kcal/mol. However, as observed for H_2 treated Norit-C not exposed to O_2 (Figure 2), the majority of water adsorbs on the oxygenated surface with H_{ads} less than the heat of condensation.

Shown in Figure 5 are water adsorption isotherms for BPL dried at 175 °C, N_2 treated at 950 °C, and H_2 treated at 950 °C. Comparing identical pretreatment conditions, adsorption isotherms on BPL are qualitatively similar to those for Norit-C. Dried BPL adsorbs 5 mmol of H_2O/g of BPL, with a threshold of 0.5 P/P_s. The N_2 treated BPL adsorbs just over 1 mmol of H_2O/g of BPL at relative pressures approaching saturation, and has a threshold pressure of approximately 0.85 P/P_s. The H_2 treated BPL adsorbs only 0.2 mmol of H_2O/g of BPL, with a linear dependence on relative pressure, identical to the behavior for water adsorption on H_2 treated Norit-C. Both the dried and N_2 treated BPL samples adsorbed significantly less water than identically treated Norit-C samples. The water adsorption isotherm for dried BPL in Figure 5 reproduces well those published previously by other groups studying this carbon (**28**−**30**).

Shown in Figure 6 are microcalorimetric measurements of H_{ads} as a function of water adsorbed on BPL dried at 175 °C, N_2 treated at 950 °C, and H_2 treated at 950 °C. The H_{ads} behavior for water adsorption on BPL samples as a function of pretreatment is qualitatively similar to that on Norit-C samples. Dried BPL initially adsorbs water with H_{ads} greater than 100 kcal/mol, but H_{ads} decreases with further adsorption to approximately 20 kcal/mol at 0.1 mmol of H_2O/g of BPL and approaches the heat of condensation by 1 mmol of H_2O/g of BPL. Further adsorption on dried BPL, corresponding to 1 to 5 mmol of H_2O/g of carbon, takes place with H_{ads} equal to the heat of condensation.

BPL treated with N_2 at 950 °C initially chemically adsorbs water with H_{ads} greater than 80 kcal/mol. Heats of adsorption drop upon further water adsorption to between 8 and 10 kcal/mol, and remain in this range for 0.1 to 1.4 mmol of H_2O/g of BPL adsorbed, and P/P_s approaching saturation. This is in contrast to N_2 treated Norit-C, on which approximately 2 mmol of H_2O/g of carbon chemically adsorbs with H_{ads} greater than 15 kcal/mol. BPL treated with H_2 at 950 °C has initial H_{ads} values of greater than 20 kcal/mol and H_{ads} decreases with increasing water adsorption to below 10 kcal/mol for 0.1 to 0.2 mmol of H_2O/g of BPL adsorbed, and P/P_s approaching saturation.

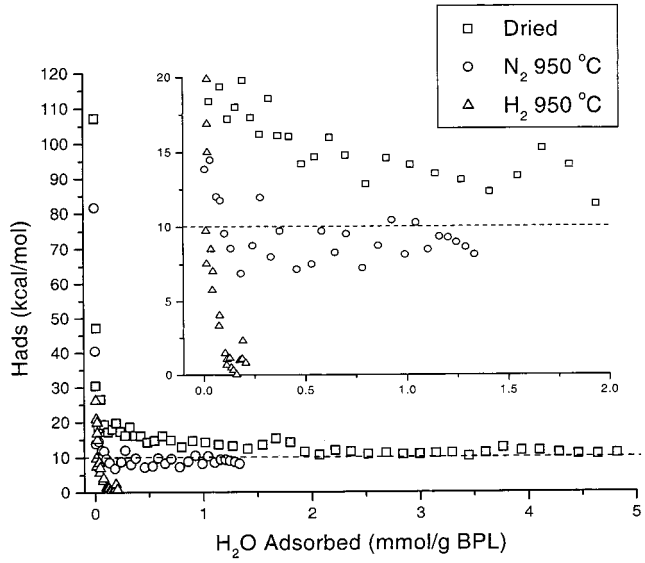

Figure 6. Heats of adsorption for water as a function of amount adsorbed on BPL carbon samples shown in Figure 5. The horizontal dashed line corresponds to the heat of condensation, and error bars are approximately given by the size of the symbols.

Several trends in comparing the H_{ads} data for Norit-C (Figure 2) and BPL (Figure 6) are notable. First, N_2 treated carbons chemically adsorb more water than H_2 treated carbons. On dried BPL however, there is no clear indication of physical adsorption with H_{ads} less than 10 kcal/mol, in contrast to the H_{ads} data exhibited for dried Norit-C. Also, for water adsorption on dried Norit-C, H_{ads} decreases from greater than 20 kcal/mol to nearly 7 kcal/mol and then increases to the heat of condensation for adsorption amounts of approximately 0.8 to 1.3 mmol of H_2O/g of carbon. This observation is commented on below. Both dried carbons exhibit adsorption isotherms and corresponding H_{ads} values consistent with a mechanism wherein most water adsorbs by condensation. Hydrogen treated BPL and Norit-C carbons each adsorb only approximately 0.2 mmol of H_2O/g of carbon, and the majority of water adsorbs with heats below those attributable to condensation.

Discussion

The data shown in Figures 1-6 can be explained within the framework of a single model. Microcalorimetric measurements indicate that there are three modes of water adsorption on carbon surfaces, which we define here to occur in an equilibrium sequence according to measured differential heats of adsorption: (i) chemical adsorption with $H_{ads} > 15$ kcal/mol, (ii) condensation with H_{ads} of approximately 10 kcal/mol, and (iii) physical adsorption with H_{ads} less than that for condensation. We note that the chemisorption of water on carbon surfaces has not previously been reported. Also, the extent of physical adsorption is seen to be significant, as noted previously (**8**−**10, 23**). Most importantly, controlling the surface chemistry determines the extent (including zero) to which each mechanism occurs. For example, carbon surfaces subjected to high-temperature H_2 treatment to eliminate PAS and active adsorption sites adsorb water by physical adsorption only. In contrast, high-temperature N_2 treatment which produce surfaces with unsaturated carbons adsorb water by all three mechanisms. Dried carbon surfaces with many PAS but no unsaturated sites adsorb water primarily by condensation and physical adsorption.

Water adsorption on N_2 treated Norit-C occurs by chemical adsorption, condensation, and physical adsorption. Initial heats

of adsorption on this sample are greater than 90 kcal/mol, and are attributed to chemical adsorption at unsaturated carbon sites (dangling radicals) produced by the pretreatment process (**12−14**). Indeed, the amount of chemically adsorbed water here is similar to the amount of oxygen that chemically adsorbs on equivalent samples.

Condensation dominates on N_2 treated Norit-C once sites available for chemical adsorption saturate. Indeed, H_{ads} plateaus at approximately 10 kcal/mol as expected for condensation (**18**). Since the initial high temperature treatment removes oxygen functionalities from the surface it is reasonable to suggest that chemically adsorbed water is acting as PAS for condensation, as observed previously (**2**). However, only a small fraction of the chemically adsorbed water generates PAS, as the ratio of chemically adsorbed to condensed water is approximately unity. This is not altogether surprising since the efficacy of acid sites as PAS is dependent on their chemical nature and geometrical configuration (**31, 32**). Intuitively one would expect many molecules to condense around a PAS nucleated by a single adsorbed molecule. Perhaps only a small fraction of the chemically adsorbed water dissociates upon adsorption, generating PAS and leading to condensation. However, there is remaining surface area on which further adsorption with low H_{ads} occurs.

For $P/P_s > 0.7$, or adsorption of greater than 2 mmol of H_2O/g of Norit-C, H_{ads} is less than that attributable to condensation. Low H_{ads} for water adsorption are generally associated with physical adsorption. In fact, theoretical models of the adsorption of water on surfaces containing various chemical functionalities predict H_{ads} less than the heat of condensation (**2**). The higher H_{ads} for water condensation, in comparison to that observed for physical adsorption, reflects the energetics of extensive hydrogen bonding within a multilayer water environment. Thus, we postulate that low H_{ads} observed here during physical adsorption result from water/surface interactions with incomplete hydrogen bonding.

The above adsorption sequence qualitatively explains results from both Norit-C and BPL following high-temperature N_2 treatment. Quantitative differences arise since far more unsaturated carbon sites are produced on BPL than Norit-C. This is illustrated by the small amount of oxygen adsorbed on BPL after high-temperature N_2 treatment (**35**).

The influence of surface chemistry on water adsorption is seen best by contrasting results from pretreated and untreated carbon samples. Untreated carbons exhibit virtually no chemical adsorption, as these surfaces are unaffected by drying and remain saturated with oxygen-based groups that serve as PAS and facilitate condensation. It is reasonable to expect surfaces on which condensation dominates to have similar adsorption isotherms and H_{ads} curves, and dried Norit-C and BPL samples do indeed behave similarly. On dried BPL there is a sufficient density of PAS to ensure condensation over the entire surface, leaving little surface on which physical adsorption can occur. This is evidenced in the adsorption isotherm and H_{ads} data that indicate water condenses at constant P/P_s of 0.5. The adsorption isotherm for dried Norit-C behaves similarly; however, at high P/P_s, H_{ads} decreases below that expected for condensation, indicating surface area is available on which water physically adsorbs.

Nitrogen treated carbons exposed to O_2 exhibit characteristics of water adsorption similar to both dried and N_2 treated carbons. They chemically adsorb water, but less than their counterpart samples that are N_2 treated only. This is because O_2 exposure saturates a portion of the active sites. The extent of condensation on N_2 treated, O_2 exposed carbon is also revealing. Since these samples have more oxygen-based PAS than N_2 treated samples, more condensation occurs. The largest amount of condensation occurs on dried carbons, as these samples contain the highest density of oxygen-based PAS. Also, N_2 treated, O_2 exposed carbons physically adsorb more water than dried carbons but less than N_2 treated carbons.

Previous work has shown that high-temperature H_2 treatment of carbon removes PAS and high activity sites. Thus, it is not surprising that virtually no chemical adsorption or condensation is observed on these samples. It is somewhat surprising that physical adsorption is not extensive. Since physical adsorption is influenced by treatment conditions, it is likely initiated at unique sites with the appropriate surface chemistry and/or geometrical configuration. Truly passivated and annealed surfaces of H_2 treated carbons may not contain a large density of such sites.

Further evidence indicating physical adsorption is found in the shape of the adsorption isotherm. When condensation dominates, the adsorption isotherm "turns up" sharply at a threshold P/P_s (e.g., Figure 5, untreated BPL at P/P_s of 0.5). In contrast, for N_2 treated Norit-C there is a gradual increase in water adsorption for $0.25 > P/P_s > 0.85$. Considering adsorption isotherm data only, in the absence of corresponding differential H_{ads} measurements, water adsorption occurring at $P/P_s > 0.4$ on N_2 treated Norit-C may mistakenly by attributed to condensation. As such, condensation and physical adsorption of water on carbons have generally not been differentiated, most probably due to the lack of thermodynamic H_{ads} measurements.

Comparison of dried and N_2 treated Norit-C elucidates the influence of surface chemistry in affecting water adsorption. The H_{ads} data of Figure 2 shows that dried Norit-C chemically adsorbs only 10% as much water as N_2 treated Norit-C, but adsorbs 4 times the amount of water by condensation. However, on both samples, physical adsorption is evident at $P/P_s > 0.7$. This behavior is reasonable since drying at 175 °C does not remove residual oxygen surface species, while N_2 treatment at 950 °C removes surface oxygen and leaves unsaturated carbon atoms (**12−14, 25−27**). Chemical adsorption dominates at low water coverages on N_2 treated Norit-C due to high-energy interactions between water and unsaturated carbon. Chemically adsorbed water is evident on dried Norit-C, arising from water-oxygen interactions. Since adsorbed oxygen has been shown previously to act as an effective PAS it is not surprising that dried Norit-C adsorbs a large amount of water by condensation.

The H_{ads} data for water adsorption on dried Norit-C (see Figure 2) indicates a mechanism of physical adsorption on PAS. Specifically, at the transition between chemical adsorption and condensation, corresponding to adsorption of 0.4 mmol of H_2O/g of carbon, there is a decrease in H_{ads} to 7 kcal/mol. The heat of adsorption increases with additional water adsorption until H_{ads} is equal to the heat of condensation at 1.2 mmol of H_2O/g of carbon. It has been postulated previously that the adsorption of water on PAS, which must occur prior to condensation, should be evidenced by H_{ads} values that are significantly lower than the heat of condensation (**2**). We attribute the "dip" in H_{ads} values for water adsorption on dried Norit-C shown in Figure 2 to a mechanism of physical adsorption directly on primary adsorption sites. We note that adsorption behavior such as this is resolvable in the H_{ads} data collected for only this sample.

The distinction in H_{ads} between condensation and physical adsorption of water suggests differences in the bonding environments arising from each mechansim. It is generally agreed that condensation involves the nucleation at a PAS of a three-

dimensional water phase with extensive hydrogen bonding. The heat of condensation reflects this extensive hydrogen bonding between water molecules. In contrast, physical adsorption results in a single monolayer of adsorbed water, with H_{ads} determined by relatively weak interactions between water molecules and the carbon surface, or residual oxygen or hydroxyl sites on the surface. Multilayer physical adsorption would be expected to be thermodynamically equivalent to condensation.

Heats of adsorption less than the heat of condensation have been observed previously for water adsorption on carbon. Young, et al., observed (**23**) that at 0.95 P/P_s only 1/30 of a monolayer of water adsorbed on low surface area (83 m^2/g) Graphon, a nonporous carbon black. A monolayer equivalent adsorbed only for $P/P_s > 0.99$, and the majority of adsorption occurred with H_{ads} approximately 6 kcal/mol. Pierce and Smith reported (**17**) that a H_2-treated, Graphon-like carbon exhibited low water uptake with H_{ads} less than the heat of condensation. These earlier measurements of H_{ads} were based on the convolution of data from multiple fundamentally incompatible instruments, and thus are subject to large uncertainty. For example, Young, et al. (**23**), convolved integral (single point) calorimetric data obtained with an immersion instrument at $P/P_s = 1$, and differential (multipoint) vapor phase isotherms where P/P_s never exceeded 0.95.

The adsorption of a monolayer of water with H_{ads} of approximately 6 kcal/mol has also been observed (**8**−**10**) on surface hydroxyl groups of HiSil, a hydrophobic precipitated silica with a surface area of 125 m^2/g. Multilayer water adsorption took place with H_{ads} approaching the heat of condensation. It was postulated that bulk nucleation requires a favorable geometrical configuration, while chemical or physical adsorption around PAS is dependent on surface chemistry (**8**). Infrared spectroscopy confirmed that water binds 'oxygen down' on residual hydroxyl groups of the HiSil, resulting in formation of a single hydrogen-like bond, and accompanying low H_{ads} values (**9**). Water molecules bound to two surface hydroxyls exhibit restricted mobility (**10**) that possibly prohibits the formation of large water clusters with long-range ordering necessary to induce condensation.

The view that condensation, or multilayer adsorption, occurs at unique sites (PAS) is generally accepted (**33**). In fact, recent theoretical models indicate that the geometrical distribution of PAS can significantly affect the critical size for formation of a stable water droplet. In particular, it was shown that the critical size of a droplet proximal to near-neighbor oxygen sites is far less than that around single acid sites (**3**). Moreover, in the absence of PAS, critical radii are large and stable droplets are not expected to form at P/P_s below saturation. Also, it is noteworthy that there is no previous suggestion that the physical adsorption of water can occur to a significant extent. Rather, it is implicitly assumed in previous studies that adsorption occurring above the threshold P/P_s does so only by condensation.

Increases in the capacity of carbons to condense water have been observed to correlate with PAS concentration (**21, 34**), and it is frequently observed that complete pore filling does not occur until a minimum PAS density exists. Current models imply that complete pore filling will take place in any pore, or pore network, containing a PAS. Yet, it is clear that for high surface area carbons not all pores are connected. Thus, assuming a random distribution of PAS in pores, not all pores or pore networks will contain a PAS until a threshold apparent density of PAS is reached. Earlier theoretical models imply (**3**) that adjacent PAS need to be proximal to one another for complete pore filling to occur. This implies that droplets around a given PAS are restricted to a maximum size, a scenario we believe to be a physically unreasonable description of the water adsorption process.

On the basis of the measured BET area of Norit-C of 1378 m^2/g and assuming that each adsorbed water molecule occupies 25 $Å^2$, the total monolayer adsorption capacity is greater than 10 mmol of H_2O/g of Norit-C. The amount of water that physically adsorbs on N_2 treated Norit-C is within this limit dictated by monolayer formation. While an appreciable amount of water physically adsorbs, subsequent condensation atop this monolayer does not occur. We postulate that this is because the formation of a weakly bound two-dimensional water monolayer does not exhibit the extensive hydrogen bonding of condensed water clusters that form around PAS. Hence, physically adsorbed water may have a geometrical arrangement that is not conducive to further adsorption. Water cluster formation around PAS is however enabled because adsorbed water molecules are entropically stabilized at these surface sites and have greater configurational freedom to nucleate condensation.

Conclusion

An extensive matrix of microcalorimetric studies of water adsorption on carbon were carried out to test some simple hypotheses regarding the impact of surface chemistry on water adsorption. It was clearly shown that water adsorbs via three mechanisms: chemical adsorption ($H_{ads} > 12$ kcal/mol), condensation (H_{ads} approximately 10 kcal/mol), and physical adsorption ($H_{ads} < 10$ kcal/mol). The predominant adsorption mechanism is a function of carbon surface chemistry. Carbons dried in N_2 at 175 °C adsorb water predominantly by condensation, after chemical adsorption at primary adsorption sites. This finding supports previous experimental and theoretical descriptions concerning the nature of primary adsorption sites and their role in the condensation process. Carbon surface chemistry can be altered by treatment with H_2 or N_2 at high temperatures. Carbons treated with N_2 at 950 °C chemically adsorb water at unsaturated carbon sites with H_{ads} above 100 kcal/mol. A substantial amount of water adsorbed on N_2 treated carbons physically adsorbs rather than condenses. Carbons treated with H_2 at 950 °C are hydrophobic and adsorb small amounts of water, primarily by physical adsorption. Oxygenation of H_2 or N_2 treated carbons increases the capacity for water adsorption, with increases attributable to physical adsorption. This study demonstrates the utility of microcalorimetric techniques in complementing standard adsorption isotherm methods in the study of water adsorption.

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