Supporting Information to the Manuscript:

Gas-phase formaldehyde adsorption isotherm studies on activated carbon: correlations of adsorption capacity to surface functional group density

by

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S1. Procedure for nitrogen adsorption isotherm analysis. For surface area and pore size distribution analysis, nitrogen adsorption isotherms were evaluated at 77 K (ASAP 2010, Micromeritics, Atlanta GA). Activated carbon samples were de-gassed on the instrument at 250°C for 24 hours and then weighed to obtain their dry mass before nitrogen adsorption began. Surface area was calculated assuming the original Density Functional Theory model with slit shape pore geometry. Density Functional Theory, a molecular-based statistical thermodynamic theory was also used to determine the total pore volume and micropore volume, defined as the pore volume contained in pores with a diameter less than 2 nm, of the activated carbon samples.

S2. Procedure for X-ray photoelectron spectroscopic analysis. Surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS). XPS spectra were taken prior to and following adsorption experiments using an AXIS Ultra DLD (Kratos Analytical) dual anode (Mg and Al K α source) with 180° hemispherical analyser. After survey spectra were recorded from 0 to 1200 eV for each activated carbon at a pass energy of 20 eV in 1 eV steps, high resolution spectra of C 1s, O 1s, N 1s, I 3d, and K 2p lines were recorded in 0.1 eV steps at a pass energy of 20 eV. Curve-fitting was performed assuming Gaussian peak shapes after the using the Shirley algorithm to subtract background for all elemental spectra but I 3d. The I 3d line results from a doublet pair of peaks, for which linear background subtraction is favored.

S3. Procedure for Boehm titrations. The Boehm titration technique was used complementary to XPS to detect and quantify acidic and basic functional groups. A known mass (0.1 g) of activated carbon was added individually to each of four, 20mL solutions of 0.05 N sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), and hydrochloric acid (HCl). Samples were prepared in triplicate with CO_2-free water in an anaerobic chamber (Labconco, Kansas City MO) with an atmosphere of high purity nitrogen in addition to

blanks of the same volume of the same solutions containing no activated carbon. Sample vials and blanks were sealed and tumbled for five days. After equilibration, all vials were returned to the anaerobic chamber, and 10 mL aliquots of supernatant were back-titrated with either nominally 0.05 N HCl (for solutions with NaOH, $NaHCO_3$, and Na_2CO_3) or nominally 0.05 N NaOH (for solutions with HCl) using a 1000-µL electronic digital pipette (Rainin, Oakland CA). Standardization of the HCl solution with Na_2CO_3 yielded an exact concentration of 0.045 N, which was then used to standardize the NaOH titrant, found to be 0.0485 N. Acid or base titrant was added in increments as low as 0.01 mL, and uptake of acid or base was monitored simultaneously with pH (Orion). For each solution, the difference in acid or base uptake between the sample and the blank was evaluated and converted to microequivalents per square meter of surface area by first dividing the uptake of the sample by the mass of activated carbon that had been in the vial and then dividing by the specific surface area of the particular activated carbon, as determined using the DFT model discussed earlier.

Uptake for each solution corresponded to a different type or set of surface functional groups. HCl uptake corresponded to total basic surface sites. $NaHCO_3$ served as a direct measure of strong carboxylic groups. NaOH uptake corresponded to total acidic surface sites comprising carboxylic, lactonic, and phenolic groups. Na_2CO_3 corresponded to carboxylic and lactonic groups, so subtracting the Na_2CO_3 uptake from the NaOH uptake yielded the amount of weakly acidic phenols and carbonyls. By the same approach, subtracting $NaHCO_3$ uptake from Na_2CO_3 uptake provided a measure of weak carboxylic groups and lactones.

S4. Adsorption Isotherms Data

The following two tables (Table S4.1 and S4.2) contain the experimental and modeled adsorption isotherm data for water vapor and formaldehyde on three select activated carbons.

Table S4-1 Experimental and modeled adsorption isotherm data for water vapor

water vapor relative pressure [P/P_0]	equilibrium adsorption capacity [mg/g], experimental			water vapor partial pressure [P/P_0], modeled		
	ACF	**GAC1**	**GACF**	**ACF**	**GAC1**	**GACF**
0.10	0.00	0.00	0.00	0.00	0.00	0.00
0.20	10.77	7.96	25.01	0.1919	0.2196	0.1975
0.30	53.17	10.96	71.25	0.3174	0.2644	0.2984
0.40	131.01	38.59	143.92	0.3966	0.4300	0.3932
0.50	223.87	77.14	176.93	0.4935	0.4919	0.5130
0.60	281.57	172.35	190.35	0.5733	0.5685	0.6064
0.70	360.94	283.94	199.00	0.7310	0.7273	0.6960
0.80	394.97	315.36	204.47	0.8274	0.8101	0.7725
0.90	404.32	334.68	211.61	0.8584	0.8771	0.9091

Table S4-2 Experimental and modeled adsorption isotherm data for formaldehyde

formaldehyde relative pressure [ppm_v]	equilibrium adsorption capacity [mg/g], experimental			formaldehyde concentration [ppm_v], modeled		
	ACF	**GAC1**	**GACF**	**ACF**	**GAC1**	**GACF**
3.65	28.20	5.30	52.30	2.6168	2.1641	3.4498
7.30	114.70	27.90	148.10	8.0107	7.9675	7.4114
10.95	260.60	93.60	223.30	9.5772	11.0575	10.9994
14.60	369.50	256.40	253.50	15.2870	12.9125	14.9012
18.25	407.10	332.70	265.50	23.2745	19.6301	17.7900
21.90	406.80	361.50	276.28	23.1674	27.0901	21.8986
25.55	402.80	362.10	282.76	21.8428	27.3241	25.6575
29.20	422.90	362.30		31.1942	27.4031	
32.85	418.30	362.40		28.3092	27.4428	

S5. Structural and chemical characteristics of activated carbon.

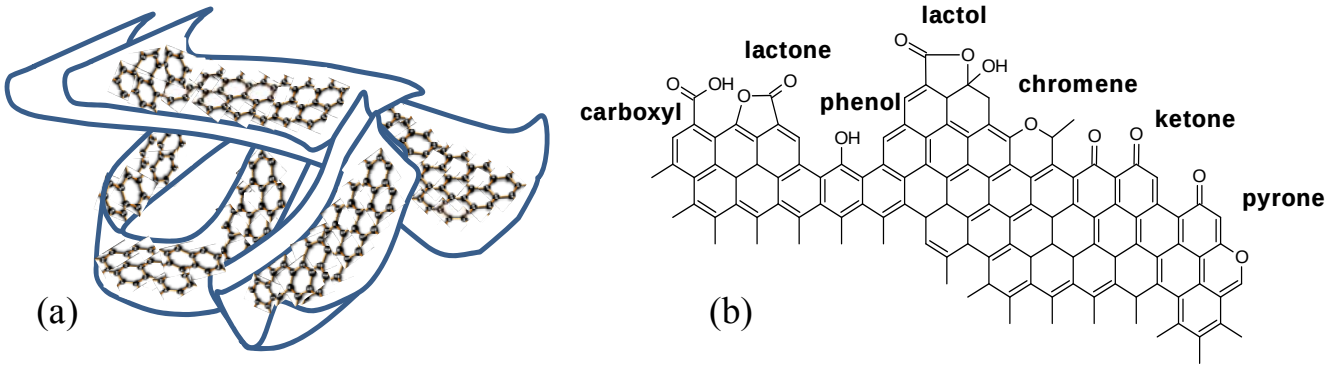

Figure S5-1. The structure (a) and representative surface functional groups (b) of activated carbon (adapted from Rodríguez-Reinoso and Molina-Sabio, 1998).

Literature Cited

Boehm, H. P. *Advanced Catalysis.* **1966**, *16*, 179-271.

Rodríguez-Reinoso, F.; Molina-Sabio, M. Textural and chemical characterization of microporous carbons. *Advances in Colloid and Interface Science*. **1998**. *76-77*, 271-294.