Supporting Information

Zeolite-Templated Carbon Catalysts for Adsorption and Hydrolysis of Cellulose-Derived Long-Chain Glucans: Effect of Post-Synthetic Surface Functionalization

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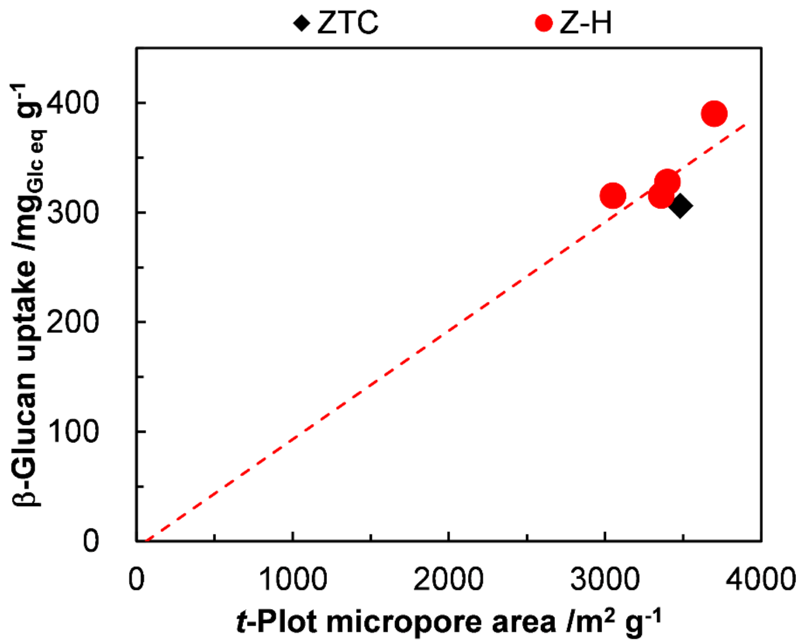

Figure S1. β-Glucan uptake of parent ZTC and Z-H materials as a function of *t*-plot micropore area.

As demonstrated with Z-N(30) and Z-S(30) in Table 1, the narrow micropores of ZTC materials are unable to take β-glucan strands in, which results in a non-zero intercept in Figure S1. This trend is identical to non-zero intercepts in our previous studies consisting of mesoporous carbon nanoparticles as well as unfunctionalized ZTC materials.[S1,S2]

Figure S2. Effect of reaction time on adsorbed β-glucan hydrolysis on Z-H(30). *Others* include mannose, fructose, and HMF. Reaction conditions: β-glucan/Z-H(30) *ca.* 25 mg; water 1 mL; 453 K; 440 rpm.

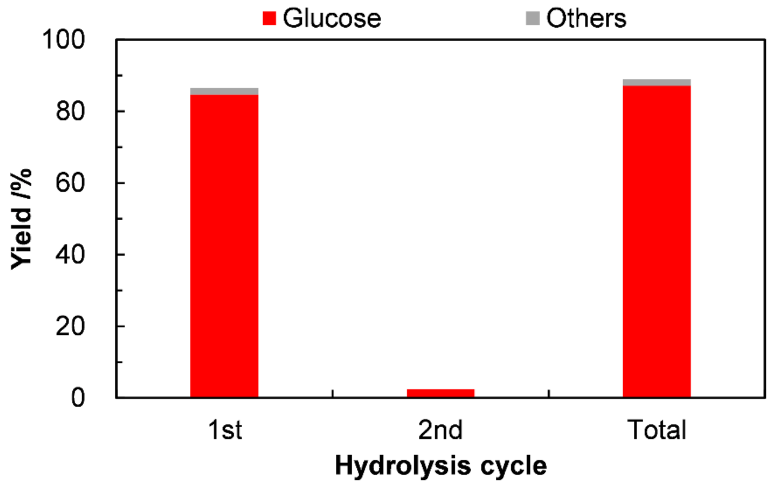

Figure S3. Product yields in two cycles of adsorbed β-glucan hydrolysis on Z-H(30). *Others* include mannose, fructose, and HMF. In the second cycle, the residue consisting of unreacted β-glucan and Z-H(30) in the first run was employed without adding either fresh substrate or catalyst, and product yields were calculated on the basis of β-glucan amount in the first cycle. Reaction conditions: β-glucan/Z-H(30) *ca.* 25 mg; water 1 mL; 453 K; 3 h; 440 rpm.

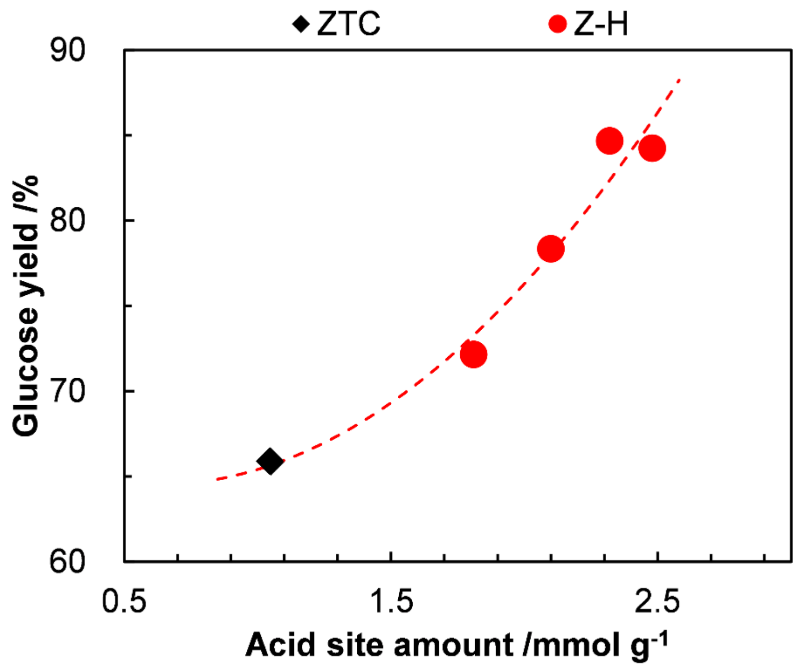

Figure S4. Glucose yield in adsorbed β-glucan hydrolysis on parent ZTC and Z-H materials as a function of acid site amount. Reaction conditions: β-glucan/ZTC *ca.* 25 mg; water 1 mL; 453 K; 3 h; 440 rpm.

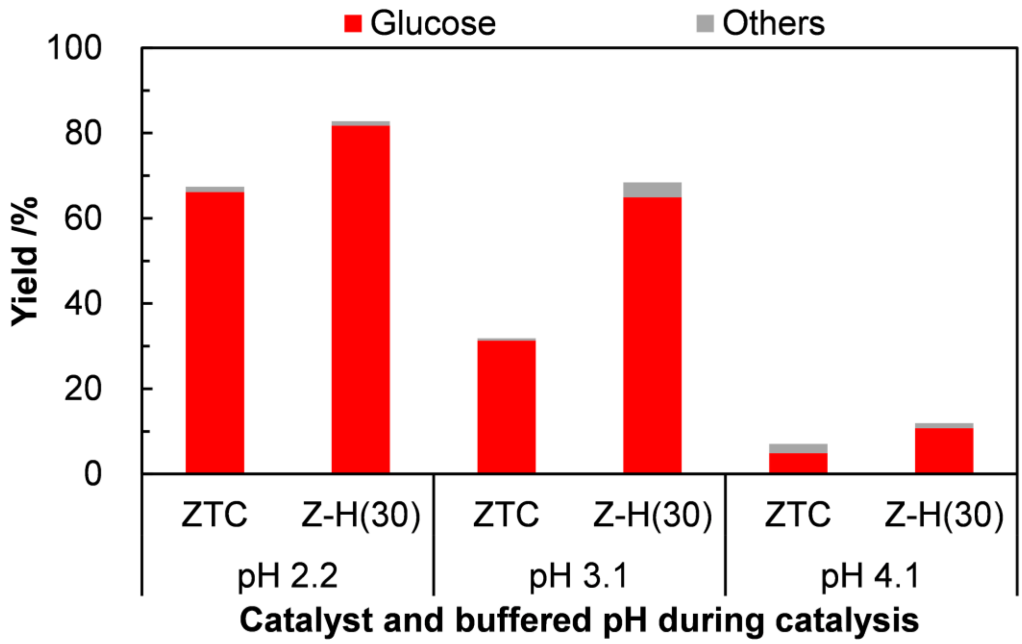

Figure S5. Adsorbed β-glucan hydrolysis on parent ZTC and Z-H(30) in buffer solutions. *Others* include mannose, fructose, and HMF. Reaction conditions: β-glucan/ZTC *ca.* 25 mg; solvent 1 mL; 453 K; 3 h; 440 rpm. The reactions at pH 2.2 and 3.1 were conducted in 20 mM of phosphate buffer and that at pH 4.1 was in 20 mM of acetate buffer.

Table S1. pH Values After Adsorbed β-Glucan Hydrolysis on ZTC and Z-H(30)[a]

Catalyst	Reaction media	pH after reaction
ZTC	Water	2.4
	Acetate buffer[b]	3.9
	Phosphate buffer[c]	2.8
	Phosphate buffer[d]	2.5
Z-H(30)	Water	2.3
	Acetate buffer[b]	3.9
	Phosphate buffer[c]	2.8
	Phosphate buffer[d]	2.5

[a]Reaction conditions: β-glucan/ZTC *ca.* 25 mg; solvent 1 mL; 453 K; 3 h; 440 rpm.
[b]20 mM, initial pH 4.1. [c]20 mM, initial pH 3.1. [d]20 mM, initial pH 2.2.

Data for both acetate and phosphate buffers indicates a lack of appreciable pH change under buffered conditions of catalysis here.

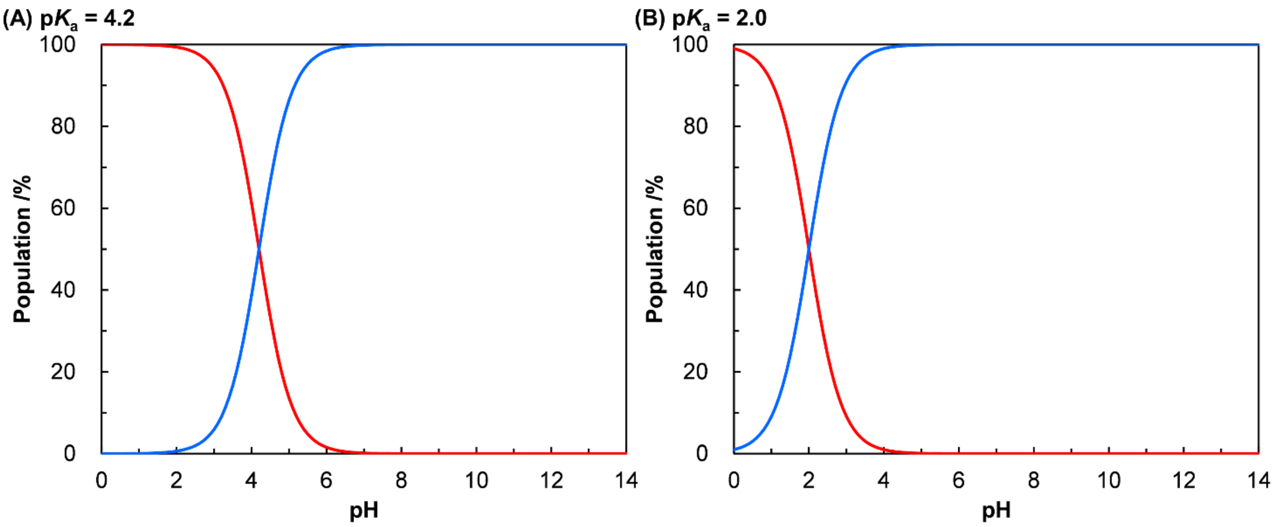

Figure S6. Population of carboxylic acid (COOH) and conjugated carboxylate (COO^-) at various pH, in the case of (A) pK_a = 4.2 as typical aromatic carboxylic acid (*i.e.*, benzoic acid)[S3] and (B) pK_a = 2.0. Legends: red line = carboxylic acid; blue line = conjugated carboxylate.

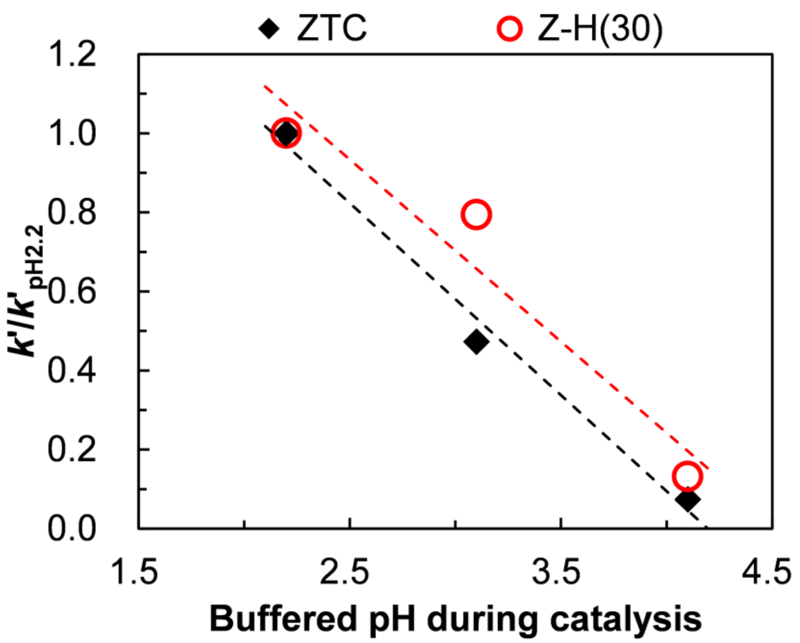

Figure S7. Ratio of pseudo-zero-order rate constants in hydrolysis of β-glucan adsorbed on parent ZTC and Z-H(30) in buffer solutions as a function of initial pH value. The pseudo-zero-order rate constant *k*′ is defined by eq. S1. Reaction conditions: β-glucan/ZTC *ca.* 25 mg; solvent 1 mL; 453 K; 3 h; 440 rpm.

$$k' = -\frac{X}{t_{\mathrm{hyd}}} \qquad \text{(S1)}$$

where X is the glucose yield and t_{hyd} is the reaction time.

References

(S1) Chung, P.-W.; Charmot, A.; Click, T.; Lin, Y.; Bae, Y.; Chu, J.-W.; Katz, A. Importance of Internal Porosity for Glucan Adsorption in Mesoporous Carbon Materials. *Langmuir* **2015**, *31*, 7288–7295.

(S2) Chung, P.-W.; Yabushita, M.; To, A. T.; Bae, Y.; Jankolovits, J.; Kobayashi, H.; Fukuoka, A; Katz, A. Long-Chain Glucan Adsorption and Depolymerization in Zeolite-Templated Carbon Catalysts. *ACS Catal.* **2015**, *5*, 6422–6425.

(S3) Jencks, W. P.; Regenstein, J. Ionization Constants of Acids and Bases. In *Handbook of Biochemistry and Molecular Biology*, 4th ed.; Lundblad, R. L.; MacDonald, F. M., Eds.; CRC Press: Cleveland, 2010.