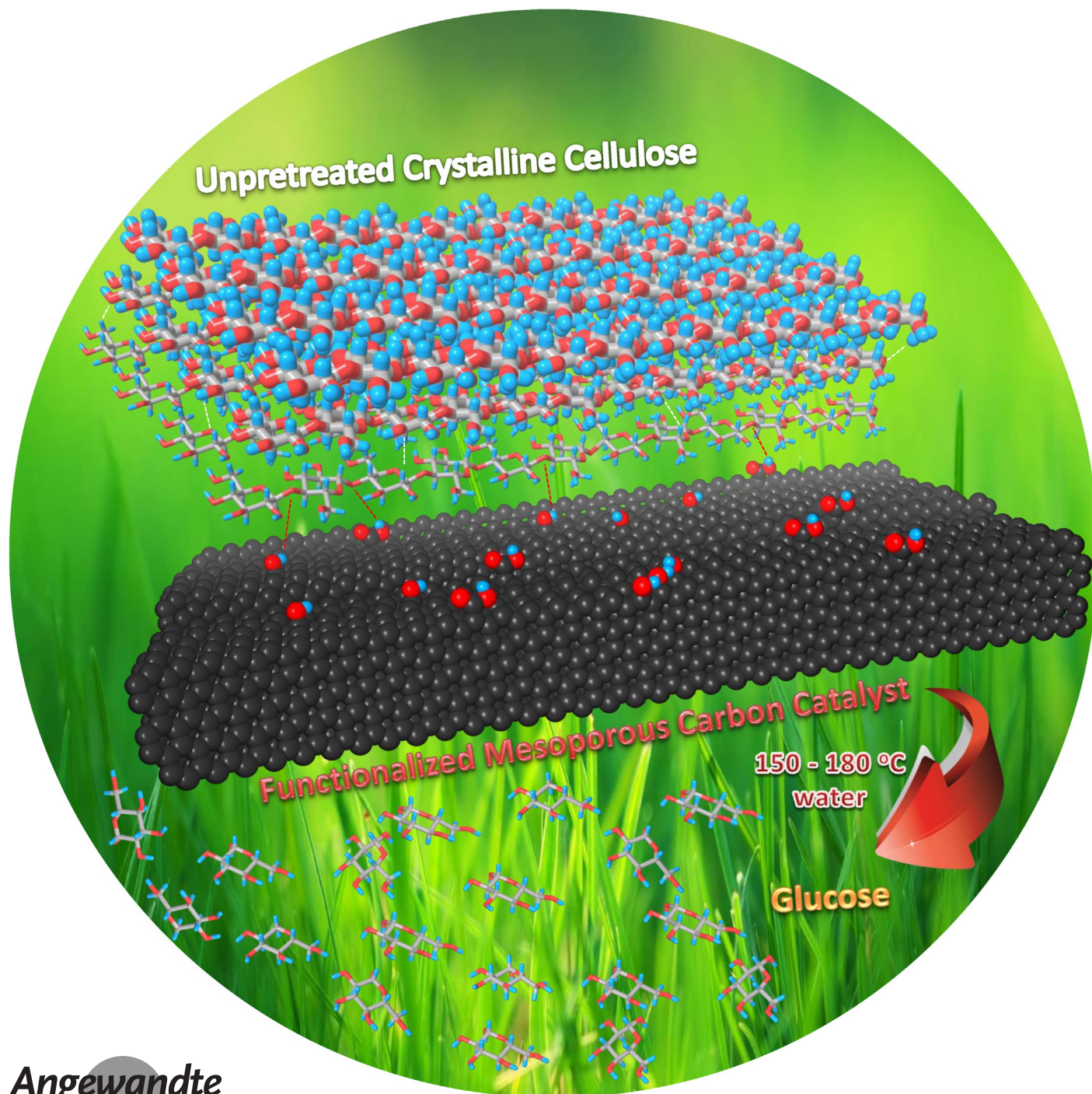


Weak-Acid Sites Catalyze the Hydrolysis of Crystalline Cellulose to Glucose in Water: Importance of Post-Synthetic Functionalization of the Carbon Surface

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Abstract: The direct hydrolysis of crystalline cellulose to glucose in water without prior pretreatment enables the transformation of biomass into fuels and chemicals. To understand which features of a solid catalyst are most important for this transformation, the nanoporous carbon material MSC-30 was post-synthetically functionalized by oxidation. The most active catalyst depolymerized crystalline cellulose without prior pretreatment in water, providing glucose in an unprecedented 70% yield. In comparison, virtually no reaction was observed with MSC-30, even when the reaction was conducted in aqueous solution at pH 2. As no direct correlations between the activity of this solid–solid reaction and internal-site characteristics, such as the β -glu adsorption capacity and the rate of catalytic hydrolysis of adsorbed β -glu strands, were observed, contacts of the external surface with the cellulose crystal are thought to be key for the overall efficiency.

Crystalline cellulose is the largest component of lignocellulosic biomass—the most abundant form of biomass on earth. Its direct catalytic hydrolysis to glucose has been historically recognized as a central bottleneck in the transformation of biomass into value-added fuels and chemicals.^[1–3] There is great interest in the development of solid synthetic catalysts that depolymerize crystalline cellulose through solid–solid interactions.^[4–11] However, to date, its recalcitrance has required pretreatment, such as using either ball milling^[4–7,11] or mixed milling,^[9,10] which adds to the number of processing steps and the energy and environmental footprint of sugar release. Indeed, thus far, only enzymes (i.e., cellulases)^[12,13] are used in practice for catalyzing the hydrolysis of crystalline cellulose to glucose in water without pretreatment. Indeed, the maximum reported yield for a synthetic chemical catalyst is below 20%,^[8] with the upper limit for a carbon catalyst being 4%.^[5] Herein, borrowing crudely from the concept of weak-acid sites that are thought to be responsible for the activity of enzymes in related catalytic hydrolysis reactions, we synthesized a carbon catalyst that overcomes prior limitations and catalyzes the hydrolysis of crystalline cellulose (i.e., Avicel) without pretreatment in water, providing soluble sugars in 70% yield, of which 96% are glucose.

Our catalyst design incorporates weak-acid sites on the carbon surface, which have previously been shown to be hydrothermally stable even in the presence of high salt concentrations.^[14,15] Our approach leverages two previously demonstrated aspects: 1) interactions between long-chain poly(1 $\rightarrow$ 4)- β -glucan (β -glu) strands derived from crystalline cellulose and the surface of the mesoporous carbon material, as driven in part enthalpically through a multitude of CH– π interactions;^[16,17] and 2) post-synthetic surface functionalization for the synthesis of a carbon catalyst surface with a high

density of weak-acid sites, which are thought to activate glycosidic oxygen atoms along the β -glu strand for hydrolysis.^[15,18]

Catalyst synthesis was performed by the post-synthetic surface functionalization of MSC-30, a high-surface-area commercially available mesoporous carbon material. Simple treatment of this material with aqueous NaOCl for various durations at controlled pH values increases the density of weak-acid sites on the surface by a factor of three to four, as shown by catalysts **T1–T4** in Table 1. Furthermore, similar enhancements in the site density were also achieved for catalyst **T5** by oxidizing MSC-30 in 1M HNO₃ solution at 105°C. Compared to the latter treatment, which is known to result mainly in carboxylic acids as the surface functional groups,^[19,20] oxidation using NaOCl occurs more mildly and results in nearly equal amounts of carboxylic acid, lactone, and phenol functional groups on the surface (Supporting Information, Figure S3). When NaOCl was used as the oxidant, increasing the treatment time under acidic conditions (where HOCl is invoked as the main oxidizing agent)^[20] led to a higher total acid-site density on the surface (**T3** vs. **T4** in Table 1). On the other hand, under basic conditions (where OCl[–] is thought to act as a weak oxidizing agent and fragment C–C bonds),^[20] the treatment time had no effect on this density (**T1** vs. **T2** in Table 1). Although such oxidative treatments are known to slightly decrease the surface area,^[14,15] which is consistent with the data in Table 1, a comparison of catalysts **T3** and **T4** shows that an extended oxidation time does not per se lead to a decrease in surface area. An analysis of the pore-size distribution in catalysts MSC-30 and **T4** shows the formation of a small fraction of larger mesopores with diameters of approximately 4 nm at the expense of those smaller than 3 nm (Figure S2).

Crucially, the acid sites in catalysts **T1–T5** are weak-acid sites, as are those in the original MSC-30 material, as confirmed by a nearly complete lack of neutralization upon treatment with a pH 4 acetate buffer. This is in stark contrast with strong-acid sites, such as surface sulfonic acid groups, which are neutralized to more than 90% after a similar treatment (Table S1).

To further characterize the internal sites of the carbon catalysts, we assessed their ability to both adsorb β -glu strands derived from cellulose as well as, in a separate experiment, to catalyze the hydrolysis of these adsorbed β -glu strands to glucose in water. This was performed by first treating each catalyst with a solution of cellulose dissolved in concentrated aqueous HCl. Such treatments have previously been shown to result in the adsorption of dissolved β -glu strands onto the internal carbon surface.^[14,16] The adsorption capacities of each catalyst after equilibration of 100 mg of the catalyst with 2.5 mL of β -glu solution (20 g L^{–1}) in concentrated aqueous acid are listed in Table 1. MSC-30 adsorbs 65% of the total β -glu amount in solution under the aforementioned conditions, leading to an adsorbed β -glu coverage of 33% (wt %) on the carbon surface. When MSC-30 and MCN, a mesoporous carbon material that previously held the record for the highest β -glu adsorption capacity, were compared under identical conditions (Figure S4), MSC-30 had a two-fold higher adsorption capacity than MCN. This is likely due to

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Table 1: Properties of MSC-30 and functionalized derivatives, and hydrolysis activity involving adsorbed β -glu strands.

Sample	MSC-30	T1	T2	T3	T4	T5
Preparation	Commercial nanoporous carbon	NaOCl, 25 °C, 2 h, pH > 12	NaOCl, 25 °C, 24 h, pH > 12	NaOCl, 25 °C, 2 h, pH 4–5	NaOCl, 25 °C, 24 h, pH 4–5	HNO ₃ (1 M), 105 °C, 1.5 h
Acid-site density ^[a] [mmol g ⁻¹]	0.5	1.6	1.6	1.9	2.2	2.2
BET surface area ^[b] [m ² g ⁻¹]	2804	1875	2399	2043	2015	1973
β -glu adsorption capacity ^[c] [mg _{glucan} /g _C]	328	161	215	175	176	189
Maximum glucose yield [%] ^[d]	61.5	82.1	77.1	79.4	91.4	68.9

[a] Measured by acid–base back titration with NaOH and HCl solutions (0.01 N). [b] The BET surface area was calculated using N₂ isotherm data within $0.01 < P/P_0 < 0.1$. [c] The concentration of the hydrolyzate solution was 20 g L⁻¹, and the mass ratio of dissolved β -glu to C was 0.5. [d] The reaction conditions are described in Figure 1. The maximum glucose yield corresponds to the total amount of glucose, cellobiose, other C₆ sugars, and HMF in solution after hydrolysis of adsorbed β -glu strands. The typical distribution of these components was 96 % glucose, 1 % cellobiose, < 0.1 % HMF, and 3 % other C₆ sugars for all reactions.

the higher surface area of MSC-30. Likewise, in part because of their lower surface area, catalysts **T1–T5** exhibited β -glu capacities that were lower than that of MSC-30 by 50–65 % (Table 1). However, other factors aside from the surface area could also play a role, such as the more polar nature of the carbon surface after oxidation, which could disfavor the release of water—a known entropic driving force for β -glu adsorption.^[17]

To further characterize the abilities of the catalysts to depolymerize adsorbed β -glu strands, a treatment in hot water at 180 °C was performed. The major product was glucose (representing 96 % of all observed species in solution according to HPLC analysis) for all catalysts.

The kinetics of glucose release in solution during the hydrolysis of adsorbed β -glu are illustrated in Figure 1. These data show a clear correlation between how fast a material catalyzes the hydrolysis of adsorbed β -glu and the maximum glucose yield. This is likely a consequence of avoiding sequential-reaction side products after glucose release by catalytic hydrolysis during short contact times. From this perspective, catalyst **T4** achieved the highest glucose yield of 91.4 %, after two hours of hydrolysis (Figure 1). In comparison, the maximum glucose yield achieved with MSC-30 was 61.5 %, after three hours of hydrolysis. Reusing a sample of catalyst **T4** for a second hydrolysis cycle (corresponding to two more hours of hydrolysis at the same temperature) led to a total glucose yield of 96.8 % (see Figure S5), thus nearly closing the mass balance. This high catalytic activity can be compared with that of MSC-30, which lacks additional weak-acid sites created by post-synthetic oxidation and only achieved a total glucose yield of 63.3 % after these two cycles. Two hydrolysis mechanisms are thus possible: a surface acid–base bifunctional mechanism^[21] in which carboxylate bases function cooperatively with phenolic OH acid sites in **T4**,^[22] or a mechanism that is solely based on the acid sites, as demonstrated for the intramolecular catalysis of the hydrolysis of glycosidic bonds.^[23]

The results achieved with **T4** and MSC-30 led us to attempt to use both of them directly as catalysts for the

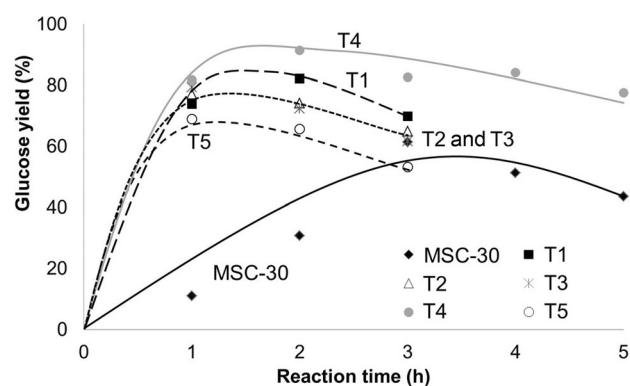


Figure 1. Evolution of the glucose yield with reaction time during hydrolysis of adsorbed β -glu strands on MSC-30 and functionalized catalysts. Reaction conditions: 15–20 mg of the indicated material in 1 mL of water, 180 °C. The glucose yield corresponds to the total amount of glucose, cellobiose, other C₆ sugars, and 5-hydroxymethylfurfural (HMF) in solution after hydrolysis of adsorbed β -glu strands. Trend lines are used for clarity and were not obtained by kinetic calculations.

depolymerization of crystalline cellulose without pretreatment in water. Testing was performed by treating 20 mg of the carbon catalyst with 1.5 mg of crystalline cellulose under stirring at 150 °C for 24 hours, followed by another 3 hours at 180 °C (Figure 2). Under these conditions, whereas **T4** hydrolyzed crystalline cellulose to provide glucose in a yield of 70 % (36 % yield after the initial 24 h at 150 °C), virtually no hydrolysis was observed in the absence of catalyst in water. Even when H₂SO₄ was added (resulting in a pH 2 solution), glucose was only formed in 6 % yield in the absence of a carbon catalyst. Similar results were achieved with MSC-30 as the catalyst, which only achieved a glucose yield of 7 % as the best result, upon addition of H₂SO₄ (pH 2). These low yields are due to the inactivity of specific-acid catalysts at such a high pH value for cellulose hydrolysis,^[24] rather than any degradation reactions. Interestingly, although catalyst MSC-30 is superior to **T4** in terms of the β -glu adsorption capacity and has an initial rate of hydrolysis of adsorbed β -glu strands

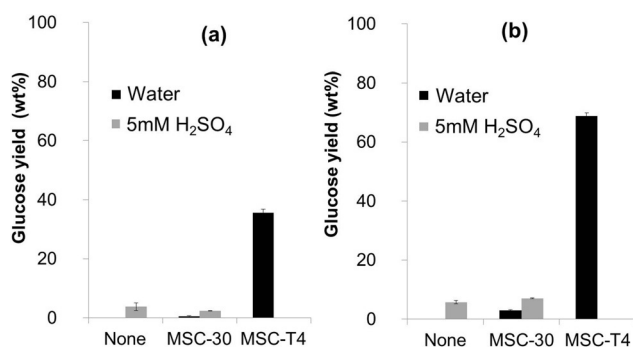


Figure 2. Direct hydrolysis of crystalline cellulose (Avicel) with different MSC-based catalysts a) at 150 °C for 24 h and b) at 150 °C for 24 h followed by 3 h at 180 °C. Reaction conditions: a solid mixture of carbon and Avicel (ca. 20 mg C and 1.5 mg Avicel) in 1 mL of water or 5 mM aqueous H₂SO₄ solution. “None” refers to control reactions lacking a catalyst in water or 5 mM H₂SO₄ aqueous solution.

that is only four times lower than that of **T4** (Figure 1), MSC-30 is a much less active catalyst of the hydrolysis of untreated cellulose than **T4**, by factors of more than 20 after the first 150 °C treatment as well as after the subsequent 180 °C treatment. The extreme difference between MSC-30 and **T4** in the depolymerization of crystalline cellulose in water can be rationalized by a higher local density of external weak-acid sites for the latter catalyst. This is indirectly reflected by a significantly more negative zeta potential in water for catalyst **T4** than for MSC-30 (see Table S2).

In summary, we have demonstrated that oxidative post-synthetic surface functionalization leads to a carbon catalyst that enables the depolymerization of crystalline cellulose without pretreatment in water, providing glucose in 70 % yield. Comparisons with a control parent material lacking this functionalization demonstrate the absence of correlations between the catalyst activity for crystalline cellulose depolymerization and 1) the β -glu adsorption capacity, as well as 2) the relative activities for the hydrolysis of adsorbed β -glu strands. Instead, this comparison strongly suggests the importance of a high local density of weak-acid sites on the external surface as the predominant factor that controls catalyst activity. These sites endow the post-synthetically functionalized catalyst with a more negative zeta potential than the control compound, and can be in direct solid–solid contact with the crystalline-cellulose surface for catalyzing the depolymerization reaction.

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- [1] C. E. Wyman, *Annu. Rev. Energy Environment* **1999**, *24*, 189–226.
- [2] E. Lam, J. H. T. Luong, *ACS Catal.* **2014**, *4*, 3393–3410.
- [3] J. R. Ziolkowska, *Biotechnol. Rep.* **2014**, *4*, 94–98.
- [4] A. Onda, T. Ochi, K. Yanagisawa, *Green Chem.* **2008**, *10*, 1033–1037.
- [5] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, *J. Am. Chem. Soc.* **2008**, *130*, 12787–12793.
- [6] A. Onda, T. Ochi, K. Yanagisawa, *Top. Catal.* **2009**, *52*, 801–807.
- [7] J. Pang, A. Wang, M. Zheng, T. Zhang, *Chem. Commun.* **2010**, *46*, 6935–6937.
- [8] Z. Fang, F. Zhang, H. Y. Zeng, F. Guo, *Bioresour. Technol.* **2011**, *102*, 8017–8021.
- [9] H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita, A. Fukuoka, *ACS Catal.* **2013**, *3*, 581–587.
- [10] M. Yabushita, H. Kobayashi, K. Hara, A. Fukuoka, *Catal. Sci. Technol.* **2014**, *4*, 2312–2317.
- [11] X. Zhao, J. Wang, C. Chen, Y. Huang, A. Wang, T. Zhang, *Chem. Commun.* **2014**, *50*, 3439–3442.
- [12] P. V. Harris, F. Xu, N. E. Kreel, C. Kang, S. Fukuyama, *Curr. Opin. Chem. Biol.* **2014**, *19*, 162–170.
- [13] X. Meng, A. J. Ragauskas, *Curr. Opin. Biotechnol.* **2014**, *27*, 150–158.
- [14] A. Charnot, P. W. Chung, A. Katz, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2866–2872.
- [15] P. W. Chung, A. Charnot, O. A. Olatunji-Ojo, K. A. Durkin, A. Katz, *ACS Catal.* **2014**, *4*, 302–310.
- [16] a) P. W. Chung, A. Charnot, O. M. Gazit, A. Katz, *Langmuir* **2012**, *28*, 15222–15232; b) P. W. Chung, A. Charnot, T. Click, Y. Lin, Y. Bae, J.-W. Chu, A. Katz, *Langmuir* **2015**, *31*, 7288–7295.
- [17] M. Yabushita, H. Kobayashi, J. Y. Hasegawa, K. Hara, A. Fukuoka, *ChemSusChem* **2014**, *7*, 1443–1450.
- [18] O. M. Gazit, A. Katz, *J. Am. Chem. Soc.* **2013**, *135*, 4398–4402.
- [19] Y. Otake, R. G. Jenkins, *Carbon* **1993**, *31*, 109–121.
- [20] P. Vinke, M. van der Eijk, M. Verbree, A. F. Voskamp, H. van Bekkum, *Carbon* **1994**, *32*, 675–686.
- [21] J. D. Bass, A. Solovyov, A. J. Pascall, A. Katz, *J. Am. Chem. Soc.* **2006**, *128*, 3737–3747.
- [22] B. Capon, *Chem. Rev.* **1969**, *69*, 407–498.
- [23] B. Capon, M. C. Smith, E. Anderson, R. H. Dahm, G. H. Sankey, *J. Chem. Soc. B* **1969**, 1038–1047.
- [24] R. Rinaldi, N. Meine, J. vom Stein, R. Palkovits, F. Schüth, *ChemSusChem* **2010**, *3*, 266–276.

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