Electronic Supplementary Information

Quantitative evaluation of ball-milling effects on the hydrolysis of cellulose catalysed by activated carbon

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Figures:

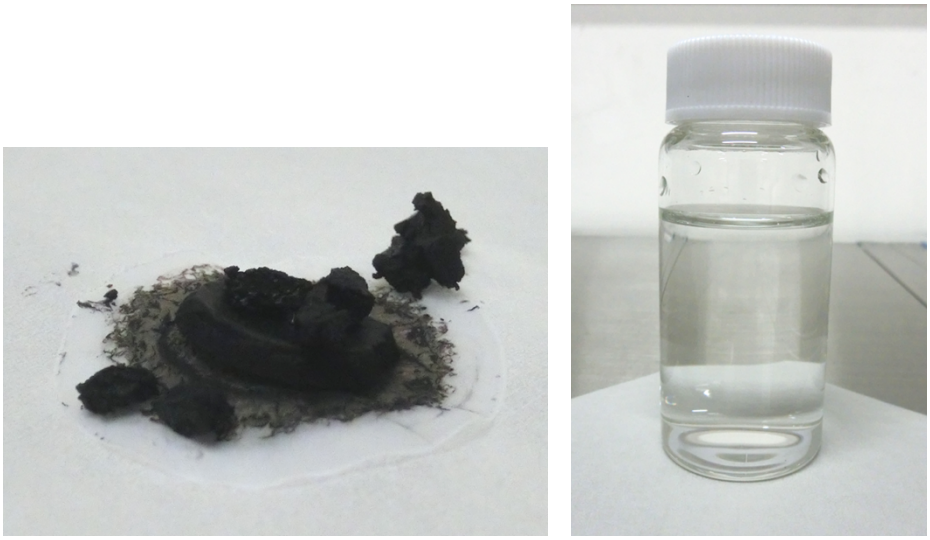

Fig. S1 Solid residue (left) and liquid phase (right) of the reaction mixture after the hydrolysis of mix-milled cellulose containing K26.

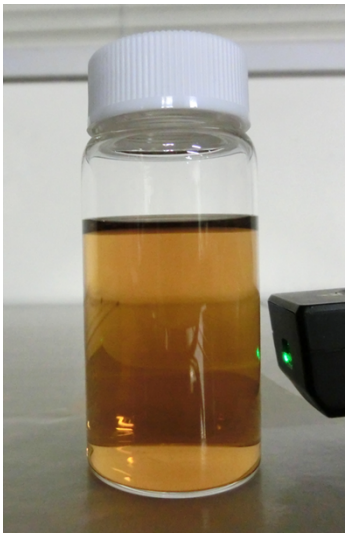

Fig. S2 Liquid phase of the reaction mixture after the hydrolysis of mix-milled cellulose containing Amberlyst. The solution was irradiated with a laser, but the Tyndall effect was hardly observed.

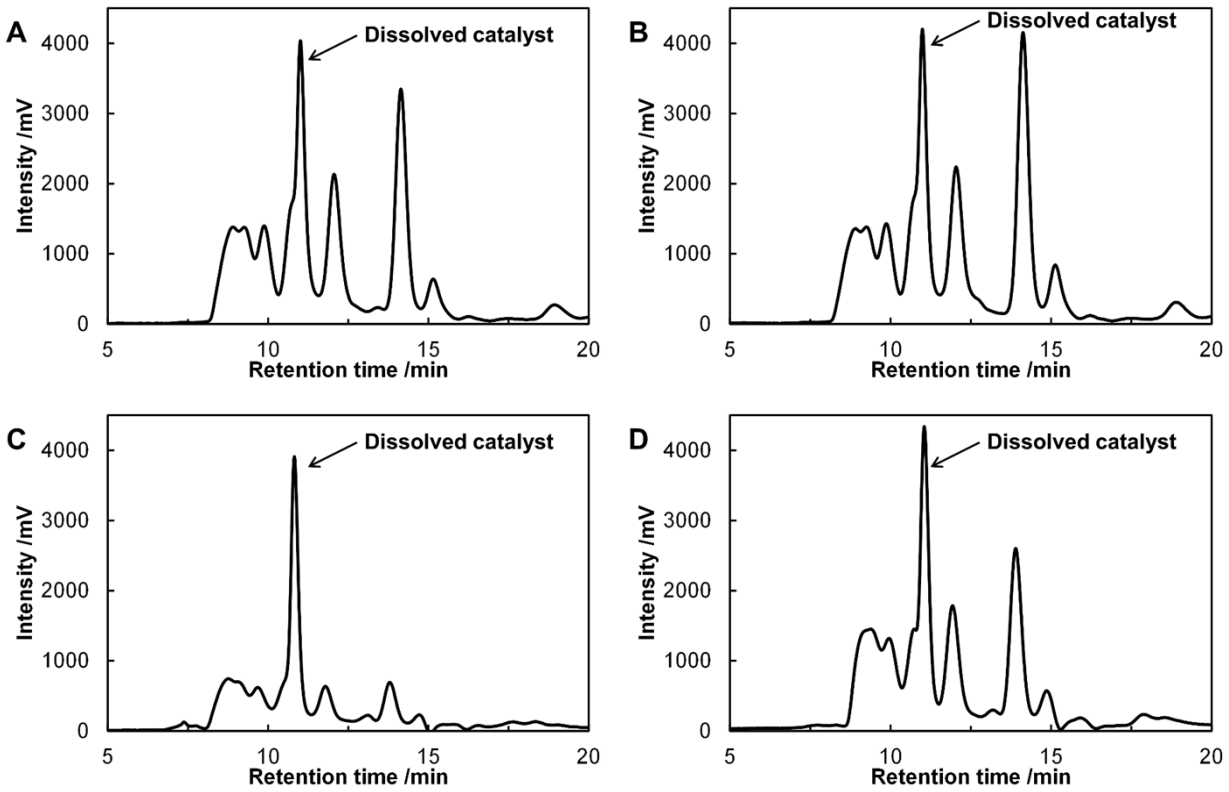

Fig. S3 HPLC charts for the hydrolysis of mix-milled cellulose containing (A) H-ZSM-5, (B) H-MOR, (C) SiO_2-Al_2O_3 and (D) SiO_2. Column: Phenomenex Rezex RPM-Monosaccharide Pb++, detector: refractive index.

Retention times: cellohexaose (8.98 min), cellopentaose (9.35 min), cellotetraose (9.90 min), cellotriose (10.7 min), cellobiose (12.1 min) and glucose (14.2 min).

Table:

Table S1 Hydrolysis of individually-milled cellulose by solid catalysts.[a]

Entry	Catalyst	*T* /K	Time /h	Conv. /%	Yield based on carbon /%C						
					Glucan		By-product				
					Glc[b]	Olg[c]	Frc[d]	Man[e]	Lev[f]	HMF[g]	Others[h]
1[S1]	None	453	0.33	12	1.3	6.6	0.2	0.2	< 0.1	0.2	3.4
16[S1]	K26	453	0.33	18	2.9	10	0.5	0.4	0.1	< 0.1	3.7
S1	BA	453	0.33	20	2.4	8.6	0.2	0.3	< 0.1	< 0.1	8.0
S2	SX	453	0.33	16	2.3	8.0	0.3	0.3	< 0.1	< 0.1	4.8
S3	Amberlyst	453	0.33	18	6.3	8.2	0.2	0.8	0.2	0.3	2.4
S4	H-ZSM-5	453	0.33	16	3.2	9.1	0.3	0.2	0.1	0.1	3.3
S5	H-MOR	453	0.33	17	3.8	9.6	0.3	0.3	0.1	0.2	3.0
S6	SiO_2-Al_2O_3	453	0.33	7.0	0.9	5.4	0.2	0.2	< 0.1	0.2	0.1
S7	SiO_2	453	0.33	12	2.1	8.3	0.3	0.4	< 0.1	0.2	1.1
S8	TiO_2	453	0.33	14	2.3	9.7	0.4	0.4	0.1	0.3	0.2

[a] Conditions: individually-milled cellulose 324 mg, catalyst (not milled) 50 mg, distilled water 40 mL. Cellulose was milled without catalyst. [b] Glucose. [c] Water-soluble oligosaccharides (degree of polymerisation = mainly 2–6). [d] Fructose. [e] Mannose. [f] Levoglucosan. [g] 5-Hydroxymethylfurfural. [h] (conversion) – (total yield of the characterised products).

Reference

S1. H. Kobayashi, M. Yabushita, T. Komanoya, K. Hara, I. Fujita and A. Fukuoka, *ACS Catal.*, 2013, **3**, 581-587.