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Author(s)	Yabushita, Mizuho; Kobayashi, Hirokazu; Hara, Kenji; Fukuoka, Atsushi
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Quantitative evaluation of ball-milling effect on hydrolysis of cellulose catalysed by activated carbons†

Mizuho Yabushita,^{a,b} Hirokazu Kobayashi,^a Kenji Hara^a and Atsushi Fukuoka^{*a}

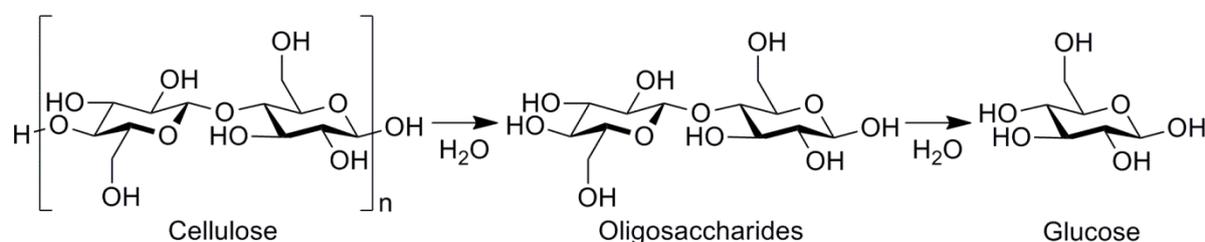
Abstract

Synthesis of glucose from cellulose is a critical roadblock for establishing a new sustainable cycle of biorefinery to produce bio-based and environmentally-benign chemicals. We have already demonstrated that a pre-treatment, ball-milling solid cellulose and solid catalyst together (mix-milling), drastically improves the yield of glucose and oligosaccharides; however, the effect of this type of ball-milling has not been quantitatively evaluated. In this study, we performed several model reactions and found that mix-milling method drastically enhanced solid-solid reactions such as hydrolysis of insoluble cellulose to soluble oligomers on the solid catalyst, but did not do liquid-solid reactions. The kinetic study indicated that the rate constant of hydrolysis of cellulose to oligomers using mix-milling increased 13-fold higher than that using individual milling. Owing to the fast depolymerisation of cellulose, we achieved 72% yield of glucose with 97% conversion of cellulose and 74% selectivity at 418 K.

1. Introduction

Cellulose is a potential alternative to petrol as this biomass is an abundant, non-edible and renewable carbon resource.¹ The monomer of cellulose, glucose, is an attractive precursor to valuable chemicals such as plastics, surfactants, high-octane-number gasoline, diesel fuels and medicines.² In addition, cello-oligosaccharides are health-promoting foods that improve bowel functions.³ Accordingly, the reaction route of cellulose to glucose and oligosaccharides

(Scheme 1) should be the mainstream in the next-generation biorefinery, which substitutes for the current processes using food biomass; however, realising this vision has been hampered by the recalcitrance of cellulose.



Scheme 1 Hydrolysis of cellulose to glucose.

The hydrolysis of cellulose has been performed with various solid catalysts, *e.g.* immobilised sulphonic acids,⁴ supported ruthenium catalysts,⁵ carbons with weak acid sites,^{5,6} highly-acidic silica,⁷ HNbMoO_6 ⁸ and hardly-soluble heteropoly acids,⁹ as heterogeneous catalysts are advantageous over homogeneous ones in terms of easy separation from products. It is surprising that weakly-acidic carbons ($\text{p}K_{\text{a}} > 3$) can hydrolyse cellulose, because usual acids with a $\text{p}K_{\text{a}}$ larger than -3 are ineffective for this reaction.¹⁰ This unexpected ability of carbons may be ascribed to the good affinity between carbon and cellulose demonstrated in model adsorption experiments using cello-oligosaccharides.¹¹ It is reported that surface-immobilised β -glucans on silica and alumina are depolymerised regardless of their weak acidity ($\text{p}K_{\text{a}} \sim 7$), whereas these weak acids do not work for the hydrolysis of free cellulose (that is, non-immobilised β -glucans).¹² These results indicate that even weak acids can function by making a good contact between the substrate and the catalyst. To increase the contact between solid catalyst and solid cellulose, cellulose and a weakly-acidic carbon catalyst (K26) were ball-milled together, denoted mix-milling.^{6a} The hydrolysis reaction of this mix-milled sample provided 90% yield of glucose and oligosaccharides in total at 453 K

in water, while that of individually ball-milled cellulose and K26 gave only 13% yield under the same conditions. This enhancement was not due to the mechanocatalytic hydrolysis¹³ during the ball-milling process, and thus the improvement of solid-solid contact was proposed. Limited collision between solid catalyst and solid substrate is a common issue for this type of reactions; however, these results suggest that this drawback can be overcome in some cases. Understanding how the mix-milling changes the reactions would be useful to design a more efficient system. Herein, the purpose of this study is the quantitative assessment of mix-milling effect on the hydrolysis by means of kinetics and model experiments.

Another remaining subject in the previous report is that the use of trace HCl is necessary for the high-yielding synthesis of glucose.^{6a} The yield of glucose was at most 57% (58% selectivity) in the reaction in pure aqueous medium under the severe conditions at 503 K with an autogenous pressure of 2.8 MPa. Accordingly, we also aimed for the selective synthesis of glucose, instead of a mixture of glucose and oligosaccharides, under mild conditions in pure water.

2. Experimental

2.1. Reagents

Microcrystalline cellulose (Avicel, 102331) was purchased from Merck and distilled water from Wako Pure Chemical Industries. The catalysts used in this work were an alkali-activated carbon (denoted K26),^{6a} a steam-activated carbon (BA, Ajinomoto Fine Techno, denoted BA), another steam-activated carbon (SX Ultra, Norit, denoted SX), a sulphonic acid cation exchange resin (Amberlyst 70, Organo, denoted Amberlyst), H-ZSM-5 [Si/Al = 45, JRC-Z5-90H, Catalysis Society of Japan (CSJ)], H-MOR (Si/Al = 45, JRC-Z-HM90, CSJ), SiO₂ (Q-6, Fuji Silysia Chemical), SiO₂-Al₂O₃ (grade 135, Sigma-Aldrich) and TiO₂ [JRC-TIO-4(2), CSJ]. Amberlyst was used after crashing on a mortar and drying overnight in

an oven at 383 K. Other reagents were obtained from Kanto Chemical and Wako Pure Chemical Industries.

2.2. Milling of cellulose and cellobiose

Microcrystalline cellulose (10 g) was ball-milled with alumina balls (1.5 cm, 2 kg) in a ceramic pot (3.6 L) at 60 rpm for 48 h. Mix-milling of cellulose and solid catalysts was carried out in the same type of pots in the presence of alumina balls. Microcrystalline cellulose (10 g) and solid catalysts (1.54 g) [substrate/catalyst (S/C) ratio based on weight = 6.5] were added into the pots and were milled together at 60 rpm for 48 h. The amount of catalyst was reduced to 1.46 g for mix-milling of cellobiose (S/C = 6.8). The ball-milled samples were analysed by powder X-ray diffraction (XRD; Rigaku MiniFlex, Cu K α).

2.3. Catalytic reactions

Hydrolysis of cellulose was conducted in a hastelloy C22 high-pressure reactor (OM Lab-Tech, MMJ-100, 100 mL). Ball-milled cellulose 324 mg, catalyst 50 mg and distilled water 40 mL were charged into the reactor. For the hydrolysis of mix-milled samples, 374 mg of the sample [containing cellulose (324 mg) and catalyst (50 mg)] and distilled water 40 mL were used. The reactor was heated to 453 K in 11 min (or 473 K in 13 min) and then cooled down to 323 K by blowing air after the reaction for *ca.* 15 min. The suspension was separated by centrifugation and decantation. The products in aqueous phase were analysed by high-performance liquid chromatography [HPLC; Shimadzu LC10-ATVP with refractive index and ultraviolet (210 nm) detectors] with a Shodex SUGAR SH-1011 column ($\phi 8 \times 300$ mm, mobile phase: water at 0.5 mL min⁻¹, 323 K) and a Phenomenex Rezex RPM-Monosaccharide Pb⁺⁺ column ($\phi 7.8 \times 300$ mm, mobile phase: water at 0.6 mL min⁻¹, 343 K). An absolute calibration method was used for the calculation of product yields.

Conversion of cellulose was determined based on the weight difference of the solid part before and after reaction. The amount of organic carbons in reaction solution was quantified by total organic carbon (TOC; Shimadzu TOC-V_{CSN}) measurement for the determination of conversion when the catalyst was partially dissolved into water after the reaction (see section 3.1).

Hydrolysis of mix-milled samples at a lower temperature (≤ 423 K) was carried out in a pressure-resistant glass tube (15 mL, Ace Glass). Mix-milled sample 94 mg [containing cellulose (81 mg) and catalyst (13 mg)] and distilled water 10 mL were charged into the tube. The tube was immersed in an oil bath at a certain temperature for a designated length of time. The analysis of products was performed by the same procedure described above.

Hydrolysis of cellobiose was conducted in the hastelloy C22 high-pressure reactor. Cellobiose 342 mg, catalyst 50 mg and distilled water 40 mL were charged into the reactor. The temperature was raised to 463 K for 11 min and then the reactor was rapidly cooled down to 323 K by blowing air. Yield of product and conversion were determined by HPLC.

3. Results and discussion

3.1. Hydrolysis of mix-milled cellulose

The activities and properties of various solid catalysts were studied in the hydrolysis of cellulose with using the mix-milling pre-treatment. As a control, the hydrolysis of ball-milled cellulose without catalyst gives a poor reaction result (7.9% yield of glucans, Table 1, entry 1), and all the catalysts tested in this study provide low yields of products without mix-milling (Table S1). Thus, hydrolysis of cellulose was performed after ball-milling together with various solid catalysts (Table 1, entries 2-10). K26 produced water-soluble glucans in 90% yield [glucose (20%) and oligosaccharides (70%)] with 97% selectivity (entry 2) as reported previously.^{6a} The other products were fructose (0.6%), mannose (0.7%), levoglucosan (0.7%),

5-hydroxymethylfurfural (1.0%) and unidentified compounds (0.1%). The solid containing the catalyst K26 was easily separated by filtration after the reaction (Fig. S1). Other carbons, BA and SX, produced glucans in 34% and 22% yields, respectively (entries 3 and 4), and they were less active than K26. Amberlyst gave the highest glucose yield (entry 5, 82%); however, the mechanocatalytic hydrolysis occurred in this case owing to strong acidity of this resin. After ball-milling cellulose and Amberlyst together, >99% of cellulose was dissolved as various kinds of oligomers^{13c} in water at room temperature. Moreover, Amberlyst was completely degraded after the hydrolysis reaction; Amberlyst was not recovered by centrifugation at 4600g or filtration using a membrane (0.1 μm mesh) and the colour of the filtrate was brown (Fig. S2). Since the Tyndall effect was hardly observed, Amberlyst presumably dissolved in water during the reaction, which was contrastive to the behaviour of K26 described above (Fig. S1). The other catalysts tested (H-ZSM-5, H-MOR, $\text{SiO}_2\text{-Al}_2\text{O}_3$, SiO_2 and TiO_2) were almost inactive (entries 6-10), and these catalysts except TiO_2 partially dissolved during the reaction (Fig. S3).

Table 1 Hydrolysis of cellulose after mix-milling pre-treatment.^a

Entry	Catalyst	<i>T</i> /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 ^{6a}	None ⁱ	453	0.33	12	1.3	6.6	0.2	0.2	< 0.1	0.2	3.4
2 ^{6a}	K26	453	0.33	93	20	70	0.6	0.7	0.7	1.0	0.1
3	BA	453	0.33	35	6.7	27	0.7	0.7	0.2	0.2	0.2
4	SX	453	0.33	24	4.2	18	0.8	0.5	0.1	0.3	0.1
5	Amberlyst	453	0.33	> 99	82	1.9	0.5	1.4	2.6	2.8	8.8
6	H-ZSM-5	453	0.33	19	4.0	11	0.4	0.3	0.1	0.2	3.2
7	H-MOR	453	0.33	21	4.9	11	0.4	0.3	0.2	0.5	4.0
8	SiO ₂ -Al ₂ O ₃	453	0.33	6.8	0.9	4.8	0.2	0.2	< 0.1	0.2	0.5
9	SiO ₂	453	0.33	16	3.4	11	0.3	0.3	0.1	0.3	0.1
10	TiO ₂	453	0.33	13	1.6	7.1	0.5	0.3	< 0.1	0.4	2.6
11	K26 ^j	418	24	97	72	2.8	1.4	1.5	1.4	4.9	13

^a Conditions: mix-milled sample 374 mg (containing cellulose 324 mg and catalyst 50 mg), distilled water 40 mL. ^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). ⁱ Ball-milling and hydrolysis of cellulose were conducted without catalysts. ^j Conditions: mix-milled cellulose 94 mg (containing cellulose 81 mg and catalyst 13 mg), distilled water 10 mL.

The correlation between crystallinity of cellulose and the result of respective catalytic reaction was estimated because the decomposition of crystalline structure of cellulose by milling treatment improves the reactivity of cellulose.¹⁴ XRD measurements represented no peak of crystalline cellulose for all the milled samples (Fig. 1), showing that cellulose was in the form of amorphous in these samples. Thus, the difference in the catalytic performance is not ascribed to the nature of cellulose but to the hydrolytic activities of catalysts and the contact between catalysts and cellulose. We conclude that K26 is the best solid catalyst for the hydrolysis of cellulose under the reaction conditions employed.

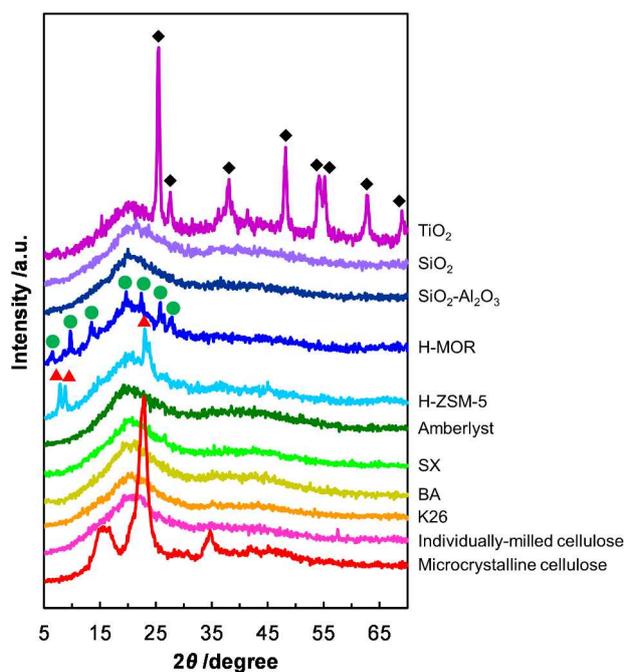


Fig. 1 XRD patterns of mix-milled samples containing cellulose and solid catalysts. The peaks marked with red triangles, green circles and black diamonds are from H-ZSM-5, H-MOR and TiO_2 , respectively.

To further improve the glucose yield, we optimised the reaction conditions for the hydrolysis of mix-milled cellulose containing K26. The yield of glucose reached 72% with 97% conversion of cellulose and 74% selectivity under the milder conditions (418 K, 24 h, 0.4 MPa of autogenous pressure; Table 1, entry 11) than that in the previous report^{6a} (503 K, 2.8 MPa, 57% yield, 58% selectivity), and the lower temperature suppressed the decomposition of glucose. The high glucose yield under the mild reaction conditions indicates the potential applicability of this catalytic process in the hydrolysis of cellulose.

3.2. Effect of mix-milling pre-treatment

The roles of mix-milling were evaluated in model reactions using soluble catalysts or substrates. If the major role of mix-milling pre-treatment is the improvement of solid-solid contact, the promotional effect of mix-milling will disappear since the use of soluble substrate

or catalyst gives a liquid-solid reaction. Therefore, we carried out the mix-milling and hydrolysis for two types of substrate-catalyst combinations: (i) cellobiose (water-soluble substrate) and K26 (insoluble catalyst) and (ii) cellulose (insoluble substrate) and benzoic acid (soluble catalyst). We chose benzoic acid as a soluble catalyst because this compound is a typical model for the active sites¹⁵ of weakly-acidic carbons. Note that a typical soluble catalyst, H₂SO₄, is not suitable for this solid-solid mixing because H₂SO₄ itself is liquid and furthermore this strong acid depolymerises cellulose during the mix-milling treatment^{13b,c}. For the combination (i), the hydrolysis of cellobiose by K26 was performed with or without the mix-milling pre-treatment. As expected, the reactions provided almost the same yield of glucose (Table 2, entries 12 and 13). For the both cases, cellobiose of *ca.* 90% dissolved into water at room temperature, and the remaining part (*ca.* 10%) adsorbed onto K26.^{11c} Therefore, the contacts between K26 and cellobiose in the both cases were the same during the hydrolysis reaction. Likewise, the combination (ii) indicated no positive effect of mix-milling, in which almost no difference in product yields was observed with or without mix-milling (entries 14 and 15). Benzoic acid completely dissolved into water at the reaction temperature. In contrast, the mix-milling pre-treatment drastically enhanced the hydrolysis with the combination of cellulose and K26; the yield of glucans was increased seven times from 13% to 90% (entries 2 and 16). Mix-milling pre-treatment accelerates solid-solid reactions but does not liquid-solid ones. These results indicate that the predominant role of the mix-milling is improvement of the solid-solid contact.

Table 2 Effect of solubility of substrate and catalyst for hydrolysis.

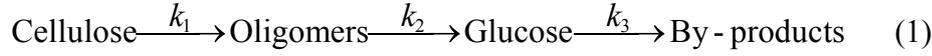
Entry	Pre-treatment	Substrate	Catalyst	Conv. /%	Yield based on carbon /%C	
					Glc ^a	Olg ^b
12 ^c	Only K26 was milled.	Cellobiose	K26	12 ^f	9.0	–
13 ^c	Mix-milling	Cellobiose	K26	14 ^f	11	–
14 ^d	Only cellulose was milled.	Cellulose	Benzoic acid	17	3.4	9.8
15 ^d	Mix-milling	Cellulose	Benzoic acid	13	2.7	8.7
16 ^{e,6a}	Individual milling	Cellulose	K26	18	2.9	10
2 ^{e,6a}	Mix-milling	Cellulose	K26	93	20	70

^a Glucose. ^b Water-soluble oligosaccharides (degree of polymerisation = mainly 2–6). ^c

Cellobiose 342 mg, K26 50 mg, distilled water 40 mL, 463 K, < 1 min. ^d Cellulose 324 mg, benzoic acid 50 mg, distilled water 40 mL, 453 K, 20 min. ^e Cellulose 324 mg, K26 50 mg, distilled water 40 mL, 453 K, 20 min. ^f Conversion of cellobiose was calculated from a total amount of recovered and adsorbed cellobiose. For the estimation of adsorbed amount of cellobiose, adsorption equilibrium constants and adsorption capacity^{11c} were used.

Kinetic study of the hydrolysis of cellulose was conducted to quantitatively estimate the effect of mix-milling, in which 418 K was chosen as the optimised temperature to synthesise glucose (see section 3.1) and accurately estimate the kinetic parameters under the steady state. Fig. 2 shows the time-course of the depolymerisation of mix-milled cellulose containing K26. The amount of cellulose (black circles) decreased, whereas that of oligosaccharides (blue squares) contrastively increased in the initial period. The yield of oligomers was maximised at 6 h (44%) and then gradually decreased as oligomers were intermediates in this reaction. With regard to glucose, a small amount of glucose (red diamonds) was simultaneously produced with oligosaccharides from cellulose, but glucose formed after accumulating oligosaccharides. The yield of glucose reached 72% at 24 h with 97% conversion of cellulose and 74% selectivity, as noted in section 3.1. Yield of glucose started to decrease after 24 h due to the decomposition as by-products (green triangles) increased. Accordingly, the hydrolysis of

cellulose consists of three steps as shown in eqn 1.¹⁶



where k_{1-3} are rate constants. We hypothesised that all steps were first-order reactions as reported elsewhere.^{14,17} The reaction rate for each step was represented as eqns (2)-(5).

$$\frac{d[\text{Cellulose}]}{dt} = -k_1[\text{Cellulose}] \quad (2)$$

$$\frac{d[\text{Oligomers}]}{dt} = k_1[\text{Cellulose}] - k_2[\text{Oligomers}] \quad (3)$$

$$\frac{d[\text{Glucose}]}{dt} = k_2[\text{Oligomers}] - k_3[\text{Glucose}] \quad (4)$$

$$\frac{d[\text{By - products}]}{dt} = k_3[\text{Glucose}] \quad (5)$$

where [Cellulose], [Oligomers], [Glucose] and [By-products] are concentrations of respective compounds and t is time. The integration of these formulae gives eqns (6)–(9).

$$[\text{Cellulose}] = [\text{Cellulose}]_0 e^{-k_1 t} \quad (6)$$

$$[\text{Oligomers}] = [\text{Cellulose}]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (7)$$

$$[\text{Glucose}] = [\text{Cellulose}]_0 \frac{k_1 k_2}{k_2 - k_1} \left\{ \frac{1}{k_3 - k_1} (e^{-k_1 t} - e^{-k_3 t}) + \frac{1}{k_3 - k_2} (e^{-k_3 t} - e^{-k_2 t}) \right\} \quad (8)$$

$$[\text{By - products}] = [\text{Cellulose}]_0 - [\text{Cellulose}] - [\text{Oligomers}] - [\text{Glucose}] \quad (9)$$

where $[\text{Cellulose}]_0$ is the initial concentration of cellulose and $k_1 \neq k_2 \neq k_3$.

Four lines in Fig. 2 represent the curve fitting with using eqns (6)–(9), which reproduced the experimental data. The determined rate constants were $k_1 = 0.17 \text{ h}^{-1}$, $k_2 = 0.16 \text{ h}^{-1}$ and $k_3 = 0.017 \text{ h}^{-1}$. The rate constant of hydrolysis of cellulose to soluble oligosaccharides was as high as that of oligosaccharides to glucose ($k_1/k_2 = 1.1$). It is surprising that k_1/k_2 exceeds 1 as the rate-determining step of the hydrolysis of cellulose to glucose is generally the first step,¹⁶ indicating that the conversion of solid cellulose to soluble oligomers was selectively accelerated by the mix-milling. In addition, high k_1/k_3 (10) and k_2/k_3 (9.4) ratios provided the good yield of glucose because the decomposition of glucose was limited.

We also performed the hydrolysis of individually-milled cellulose by K26 at 418 K instead of the mix-milled sample. Note that the reactivity itself of individually-milled cellulose should be similar to that of mix-milled cellulose, as their polymerisation degrees determined by viscometry¹⁸ (640–690), median particle diameters (12–13 μm) and crystallinity indexes ($< 5\%$) are almost the same.^{6a} Since the hydrolysis reaction was slow in this case, we analysed products by a sampling method to improve the accuracy. Formation of oligomers, subsequent production of glucose and successive decomposition of glucose were observed in this reaction. Therefore, the same curve fitting was applied to this reaction, which provided rate constants of $k_1 = 0.013$, $k_2 = 0.16$ and $k_3 = 0.017 \text{ h}^{-1}$. k_1 was greatly decreased by changing the pre-treatment from mix-milling to individual milling, while the values of k_2 and k_3 were similar regardless of the pre-treatment method. As a result, the ratio of k_1/k_2 was as small as 0.081, showing that the hydrolysis of cellulose to soluble oligomers was the rate-determining step. Consequently, we demonstrated that the mix-milling selectively and drastically increase k_1 (13-fold) in the solid-solid reaction.

A typical soluble acid H_2SO_4 was also tested as a catalyst for the hydrolysis of

individually-milled cellulose in order to compare solid-solid and solid-liquid reactions (Fig. 3). The concentration of H_2SO_4 was 50 mM (0.49%) as a usual value for the diluted H_2SO_4 processes.^{2a,19} The rate constants obtained by a curve fitting were $k_1 = 0.5 \text{ h}^{-1}$, $k_2 = 17 \text{ h}^{-1}$ and $k_3 = 0.12 \text{ h}^{-1}$. The first step is slow ($k_1/k_2 = 0.029$), indicating that hydrolysis of cellulose to soluble oligosaccharides is the rate-determining step for the production of glucose. This result is reasonable as the hydrolysis of cellulose is significantly more difficult than that of soluble oligomers.¹⁶ Therefore, the high ratio of k_1/k_2 for the hydrolysis using K26 and mix-milling is specific to this reaction, and hence we propose that the solid-solid contact created by mix-milling can selectively accelerate the solid reaction.

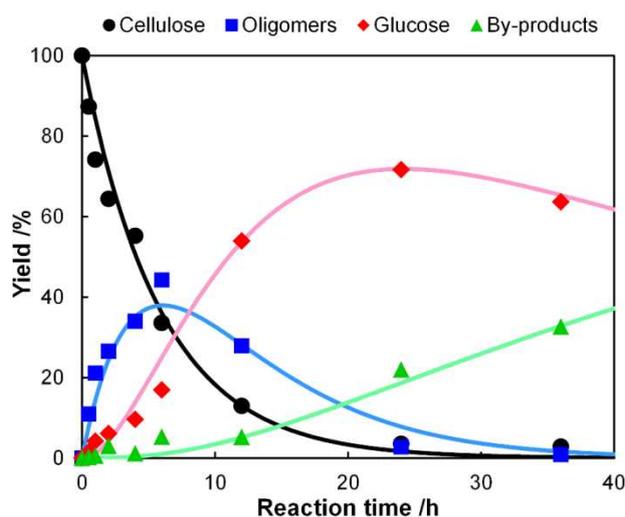


Fig. 2 Time-course of hydrolysis of mix-milled cellulose containing K26 at 418 K. The dots show the experimental data and the lines are the results of kinetic simulations based on eqns (6)–(9).

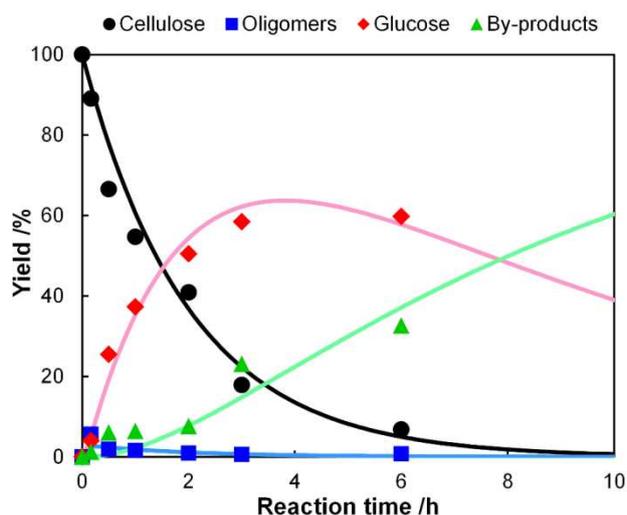


Fig. 3 Time-course of hydrolysis of ball-milled cellulose by H_2SO_4 (50 mM) at 418 K. The dots show the experimental data and the lines are the results of kinetic simulations based on eqns (6)–(9).

4. Conclusions

We evaluated the effect of mix-milling by three types of combinations: (i) insoluble cellulose and insoluble K26, (ii) soluble cellobiose and insoluble K26 and (iii) insoluble cellulose and soluble benzoic acid. Mix-milling enhanced the hydrolysis of glycosidic bonds only when the combination (i) was employed. These results indicated that solid-solid reactions were accelerated by creating better contact between solid cellulose and solid catalyst. The rate constant of hydrolysis of mix-milled cellulose to oligomers increased 13 times higher than that of individually-milled one. This high rate constant contributed to the high-yielding synthesis of glucose from cellulose (72% yield, 97% conversion and 74% selectivity) under mild conditions. We believe that the mix-milling is a promising technique for accelerating the reactions that occur at the solid-solid interface.

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Notes and references

^a *Catalysis Research Centre, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan. Email: fukuoka@cat.hokudai.ac.jp*

^b *Division of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan*

† Electronic Supplementary Information (ESI) available: Pictures of residue and reaction solutions, HPLC charts and results of hydrolysis of individually-milled cellulose. See DOI: 10.1039/b000000x/

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Electronic Supplementary Information

**Quantitative evaluation of ball-milling effect on hydrolysis of
cellulose catalysed by activated carbons**

Mizuho Yabushita,^{a,b} Hirokazu Kobayashi,^a Kenji Hara^a and Atsushi Fukuoka*^a

^a*Catalysis Research Centre, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.*

^b*Division of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.*

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.

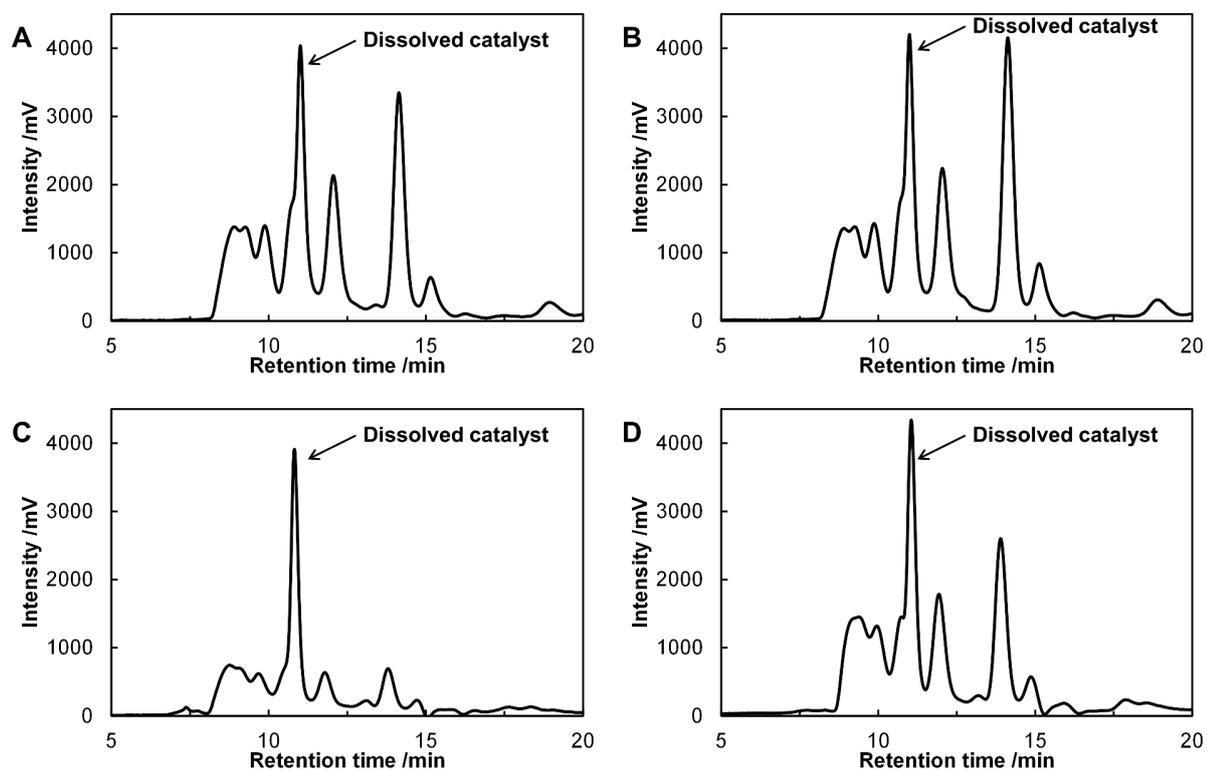


Fig. S3 HPLC charts for the hydrolysis of mix-milled cellulose containing (A) H-ZSM-5, (B) H-MOR, (C) $\text{SiO}_2\text{-Al}_2\text{O}_3$ and (D) SiO_2 . Column: Phenomenex Rezex RPM-Monosaccharide Pb^{++} , detector: refractive index.

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 ₂ O 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).

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