Supporting Information

Boosting the mechanocatalytic hydrolysis of cellulose

by using the vibratory disc mill and clay minerals

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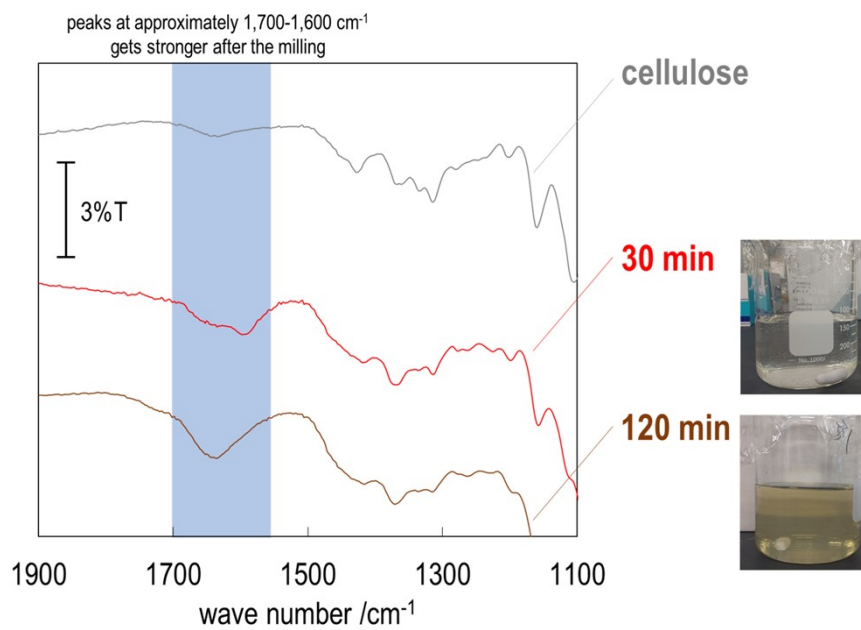** Corresponding author: Keiichiro Matsushima (matsushima-keiichiro @hro.or.jp), Tel: +81-
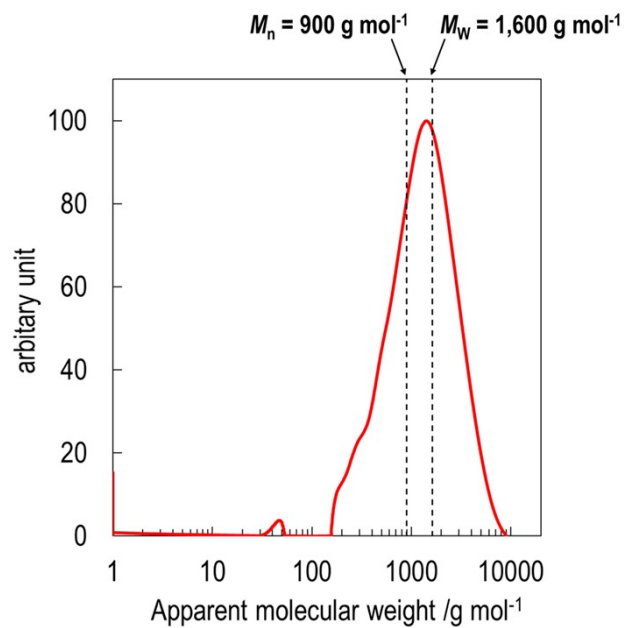
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Figure S1. FTIR spectra of the water-soluble cellulose (catalyst: kaolin, milling time: 30 and 120 min.) and powder of cellulose used as a starting material.

M_n = 900 g mol^{-1} M_w = 1,600 g mol^{-1}

arbitary unit

100

80

60

40

20

0

1   10   100   1000   10000

Apparent molecular weight /g mol^{-1}

Figure S2. A molecular weight distribution of the water-soluble cellulose in the supernatant (substrate: cellulose (1.5 g), catalyst: kaolin (1.5 g), milling time: 180 min., milling machine: vibratory disc mill). The distribution, the number average molecular weight (M_n) and the mass average molecular weight (M_w) were calculated from the chromatogram measured by SEC.

Table S1. Composition analysis of the water-soluble cellulose by X-ray fluorescence spectrometer (catalyst: kaolin, milling time: 90 min.).

element	percentage in weight /%
oxygen	58.0
carbon	26.6
silicon	9.09
aluminum	5.26
potassium	0.55
iron	0.32
sodium	0.11
chromium	0.05
calcium	0.04
sulfur	0.01

| Milling machine	Apparatus	Vessel	Milling mode
Vibratory disc mill (9306C, Rigaku)			surface grinding by shear stress
Attrition mill (PWD, Nippon Coke & Engineering)			volume grinding by impact force

Figure S3. Apparatus and milling modes of the mills used in this work (vibratory disc mill and the attrition mill)
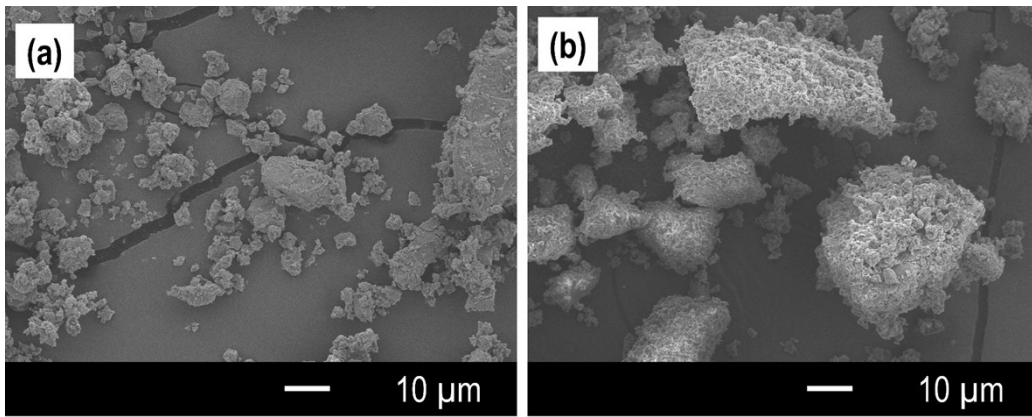
Figure S4. SEM images of the powder of cellulose and kaolin: (a) milled by the vibratory disc mill (90 min) and (b) the attrition mill (90 min).
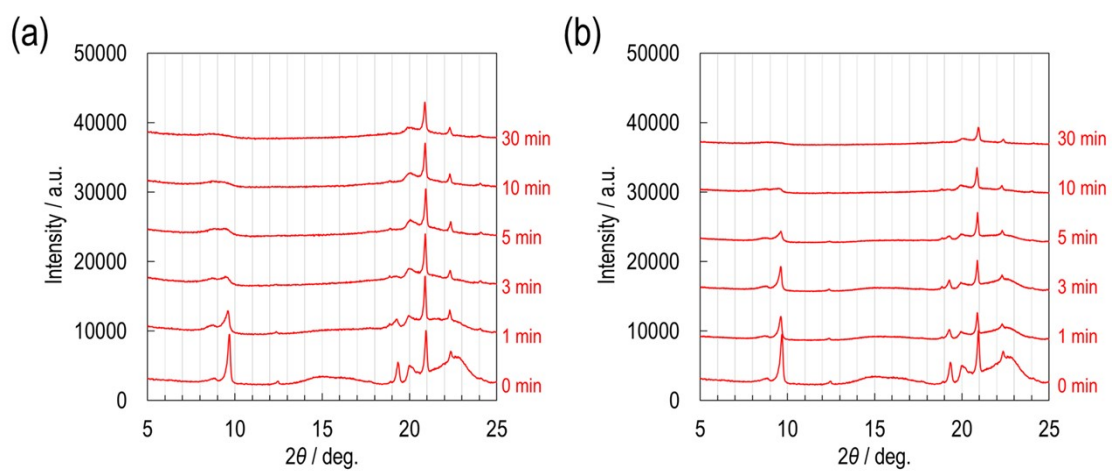
Figure S5. XRD patterns of the milled powder of cellulose and kaolin for various milling time (0-30 min): (a) the vibratory disc mill and (b) the attritor mill.
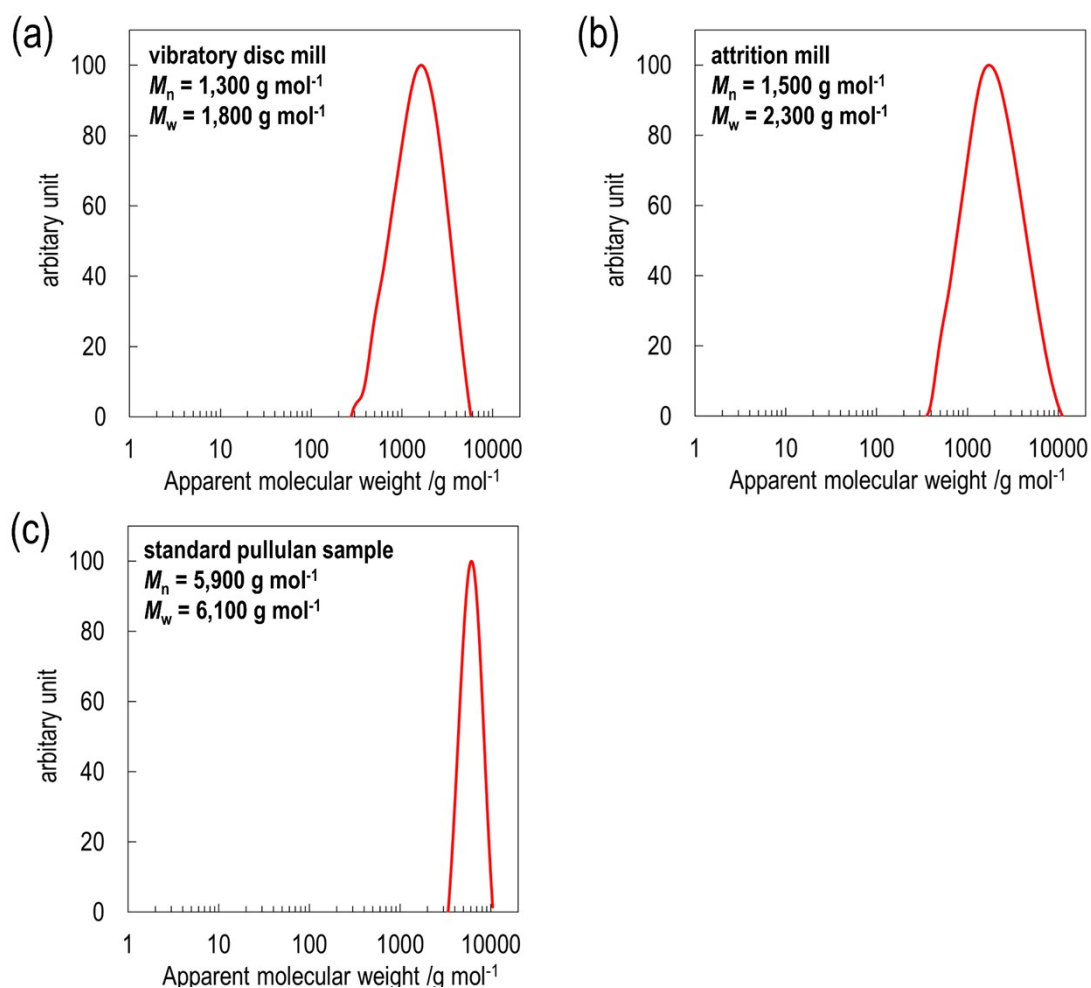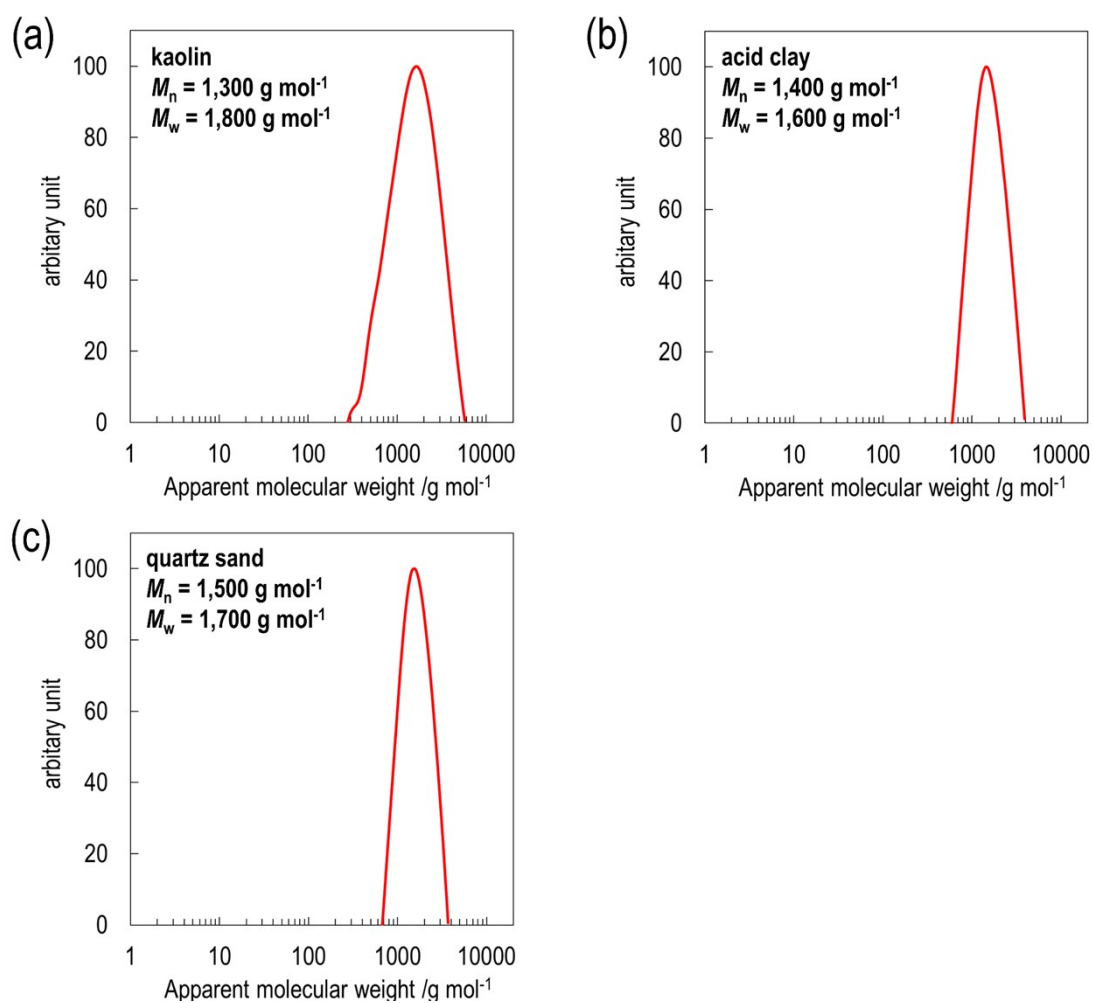
Figure S6. Molecular weight distributions of the water-soluble celluloses prepared by using various milling machines: (a) the vibratory disc mill and (b) the attrition mill (substrate: cellulose (1.5 g), catalyst: kaolin (1.5 g), milling time: 90 min). The distribution, the number average molecular weight (M_n) and the mass average molecular weight (M_w) were calculated from the chromatogram measured by HPLC. (c) is a molecular weight distribution of standard pullulan sample (a cello-oligosaccharide with a nominal M_w of 5,900 g mol^{-1}) measured as a reference.
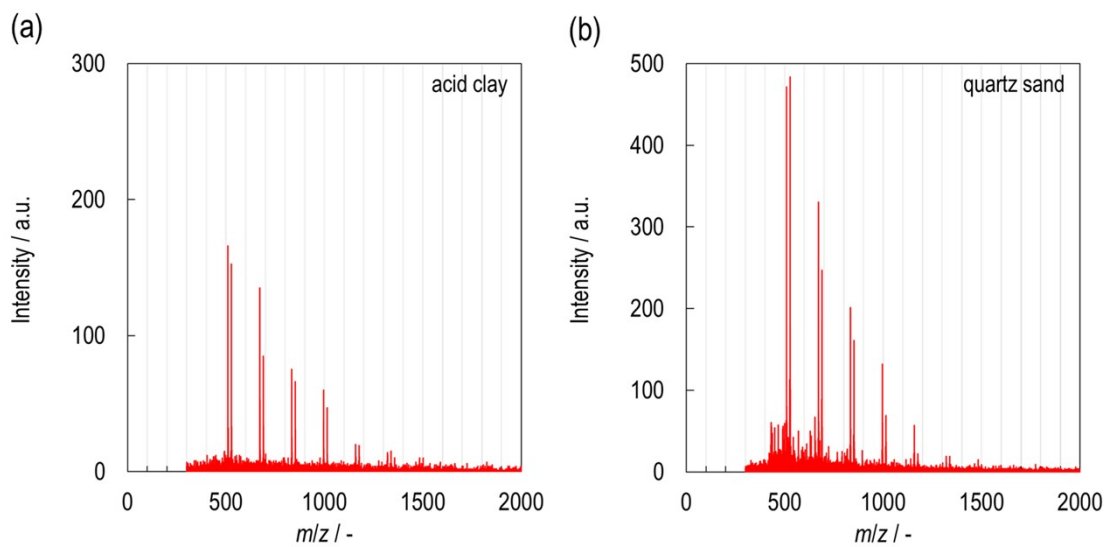
Figure S7 Mass spectra of the water-soluble celluloses (milling time: 90 min): (a) clay and (b) quartz sand.

Figure S8. Molecular weight distributions of the water-soluble celluloes prepared by using various catalysts: (a) kaolin, (b) acid clay and (c) quartz sand (substrate: cellulose (1.5 g), catalyst (1.5 g), milling time: 90 min). The distribution, the number average molecular weight (M_n) and the mass average molecular weight (M_w) were calculated from the chromatogram measured by HPLC.