Hydrolysis of cellulose using an acidic and hydrophobic ionic liquid, and subsequent separation of glucose aqueous solution from the ionic liquid and 5-(hydroxymethyl)furfural

Supporting Information

Hydrolysis of cellulose using an acidic and hydrophobic ionic liquid, and subsequent separation of glucose aqueous solution from the ionic liquid and 5-(hydroxymethyl)furfural

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Materials

Trioctylphosphine, 1-bromopentane, and potassium hydrogen phthalate were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Sodium carbonate, sulfuric acid, phosphoric acid, and hexane were purchased from Kanto Kagaku and used as received. Cellulose (Avicel PH-101) and Amberlite IRN 78 hydroxide were purchased from Sigma-Aldrich Co. LLC. and used as received.

Supporting Figures

Figure S1 shows the time course of glucose yield during hydrolysis of phosphoric acid swollen cellulose with 7.5 g of $[P_{8,8,8,5}][HSO_4]$-saturated water. The glucose yield increased and reached to 30 % after 180 min. The high yield compared to that with biphasic systems (see Figure 4 in the main manuscript) is due to supressing glucose decomposition (see Figure S2, shown below).

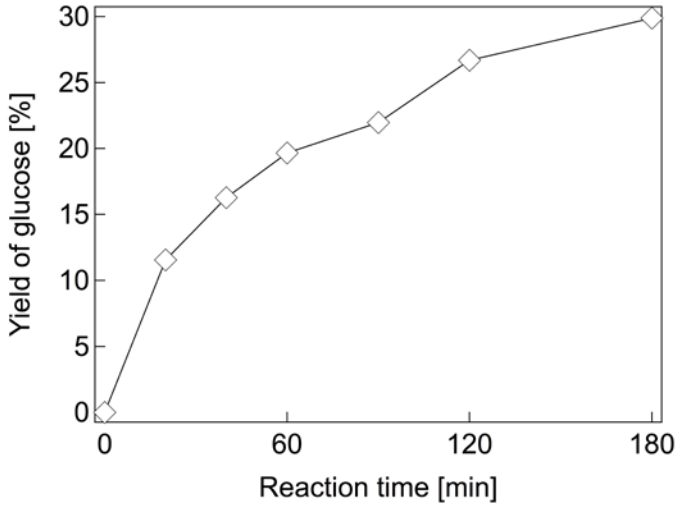

Figure S1. Time course of glucose yield during hydrolysis of phosphoric acid-swollen cellulose with 7.5 g of $[P_{8,8,8,5}][HSO_4]$-saturated water ($[P_{8,8,8,5}][HSO_4]$ amount is below 5.3 mg).

Different amounts of $[P_{8,8,8,5}][HSO_4]$ were added to 7.5 g of glucose aqueous solution (37 mM), supplying two $[P_{8,8,8,5}][HSO_4]$/water biphasic systems (2.5 or 1.0 g of $[P_{8,8,8,5}][HSO_4]$) and $[P_{8,8,8,5}][HSO_4]$-saturated aqueous solution. The decomposition rate of glucose decreased with decreasing the amount of $[P_{8,8,8,5}][HSO_4]$. Especially, the major part of glucose did not decompose in the $[P_{8,8,8,5}][HSO_4]$-saturated aqueous solution after 60 min while almost all glucose did decompose in the solution with 2.5 g of $[P_{8,8,8,5}][HSO_4]$. It indicates that the decomposition of glucose mainly occurs in IL phase or at the IL/water interface, while the decomposition may somewhat occur in the aqueous phase. Since almost all glucose was distributed in the water phase in the case of the solution with ratio of 1.0/7.5 (IL/water, by weight), the glucose decomposition should occur at the IL/water interface rather than the IL phase.

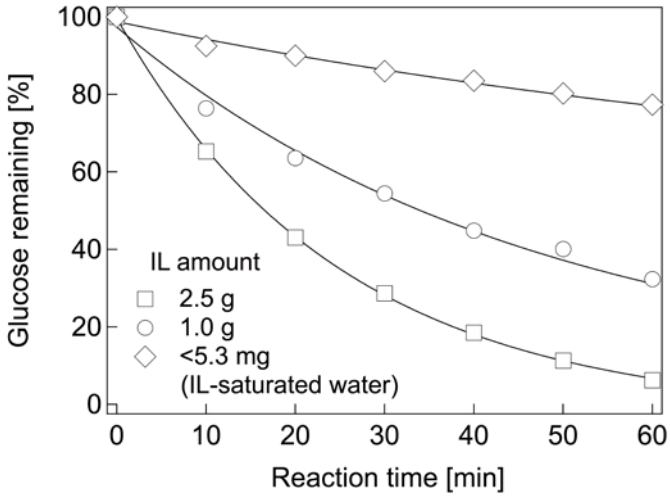

Figure S2. Degradation of glucose with different amount of $[P_{8,8,8,5}][HSO_4]$ at 190 ^{o}C.

Thermogravimetric analysis was performed with DTG-60AH (Shimadzu Co.) at a heating rate of 10 ^{o}C/min. Decomposition temperature of $[P_{8,8,8,5}][HSO_4]$ was 313 ^{o}C, showing high thermal stability. Since there is almost no degradation at 190 ^{o}C, $[P_{8,8,8,5}][HSO_4]$ should be recyclable.

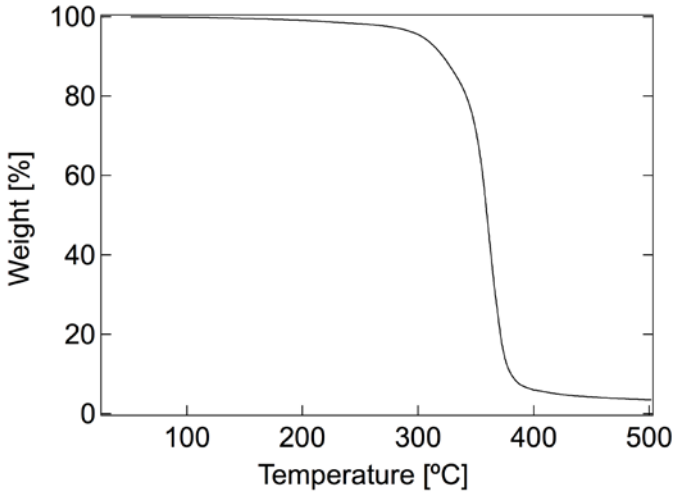

Figure S3. Thermogravimetric analysis chart of $[P_{8,8,8,5}][HSO_4]$.

Recyclability of $[P_{8,8,8,5}][HSO_4]$ was investigated. Hydrolysis proceeded even at the fourth use with a maximum glucose yield of 10.4 % after 40 min. This value was 80 % of the maximum glucose yield at first use.

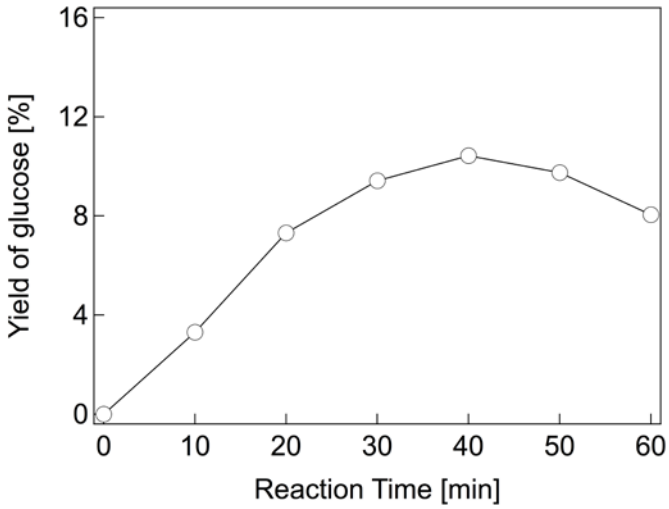

Figure S4. Time course of glucose yield during hydrolysis of phosphoric acid swollen cellulose with the biphasic system comprising the recycled $[P_{8,8,8,5}][HSO_4]$ and water under microwave heating at 190 ^{o}C. $[P_{8,8,8,5}][HSO_4]$ for this hydrolysis has been recycled three times before this hydrolysis.

Decomposition of $[P_{8,8,8,5}][HSO_4]$ during hydrolysis was investigated by ^{1}H NMR. There is no

change between the spectra of fresh $[P_{8,8,8,5}][HSO_4]$ and $[P_{8,8,8,5}][HSO_4]$ after fourth hydrolysis.

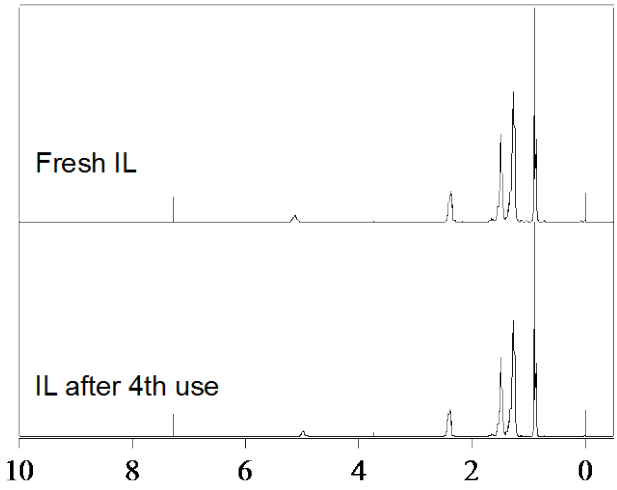

Figure S5. ^{1}H NMR spectra of fresh $[P_{8,8,8,5}][HSO_4]$ and $[P_{8,8,8,5}][HSO_4]$ after 4th use.