Electronic Supplementary Information for

A One-pot Reaction for Biorefinery: Combination of Solid Acid and Base Catalysts for Direct Production of 5-Hydroxymethylfurfural from Saccharides

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Experimental

Catalysts: Amberlyst-15 and Nafion NR50 were purchased from Aldrich Inc. SO_4/ZrO_2 was obtained from Wako Pure Chemicals. $Nb_2O_5{\cdot}nH_2O$ was supplied from CBMM. Mg-Al hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3$, was supplied from TOMITA Pharmaceutical Co. Ltd.

Transformation of saccharides:

The reaction was typically performed using 0.1 g of solid acid catalyst and/or 0.1 g of solid base catalyst, 0.1g of substrate (fructose, glucose, sucrose and cellobiose) and 3 mL of DMF at 353–393 K. Prior to the reaction, solid acid catalysts except for ion-exchange resins were evacuated at 453 K for 1 h. For ion-exchange resins (Amberlyst-15 and Nafion NR50), samples were evacuated at 353 K for 1 h. Mg-Al hydrotalcite was used as the carbonate form without pretreatment. The products were analyzed by high-performance liquid chromatography (HPLC) using a Bio-rad Aminex HPX-87H column.

Table S1. Isomerization of glucose to fructose over solid base catalysts[a]

Catalyst	Conversion /%	Yield /%	
		Fructose	HMF
Hydrotalcite	62	38	0
MgO	22	8	0
CaO	89	8	0
$Mg(OH)_2$	16	0	0
Piperidine[b]	83	5	0
Blank	0	0	0

[a]Reaction conditions: glucose (0.1 g), catalyst (0.1 g), solvent (3 mL), 373 K, 3 h [b]70 μmol

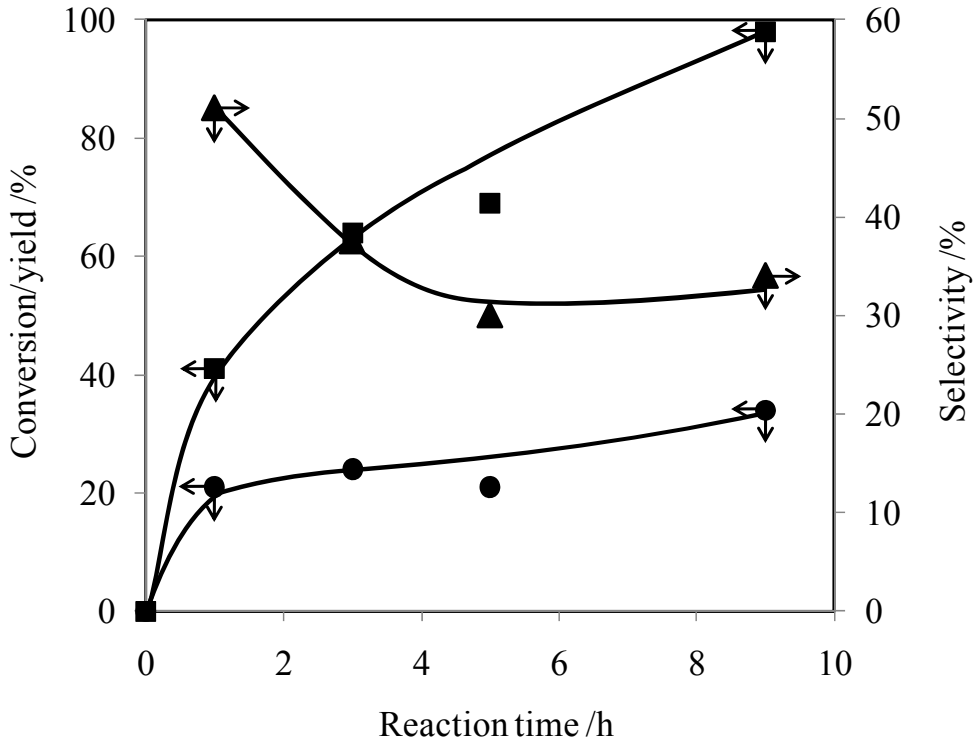

Figure S1. Plot of glucose conversion (■), 5-hydroxymethylfurfural (HMF) yield (●), and selectivity (▲) for the transformation of glucose as a function of reaction time. Reaction conditions: glucose (0.1 g), hydrotalcite (0.1 g), Amberlyst-15 (0.1 g), DMF (3 mL), 373 K.

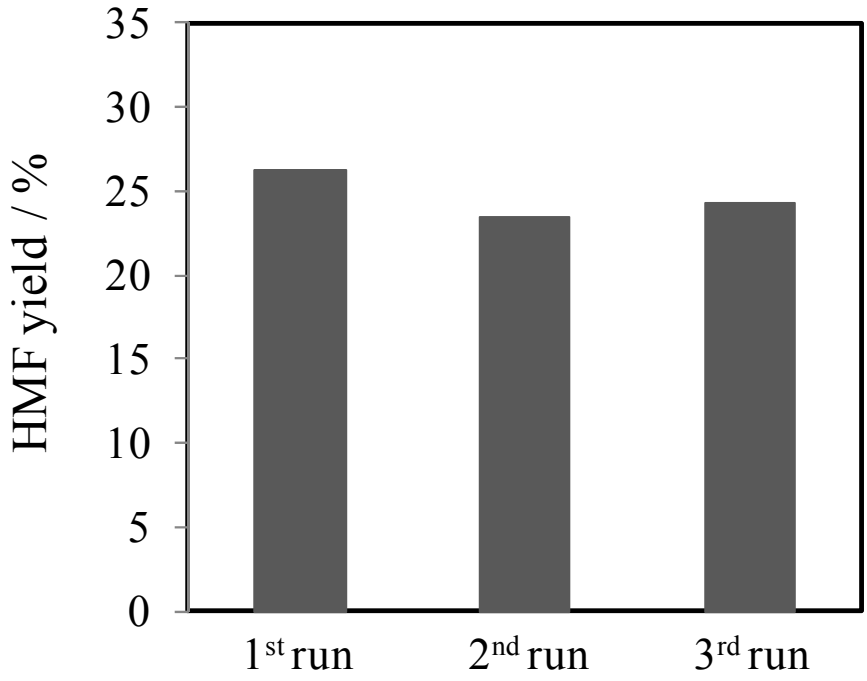

Figure S2. Yields of 5-hydroxymethylfurfural (HMF) from glucose using hydrotalcite and Amberlyst-15 for recycle use. Reaction conditions: glucose (0.1 g), hydrotalcite (0.1 g), Amberlyst-15 (0.1 g), *N*,*N*-dimethylformamide (3 mL), 373 K, 3 h

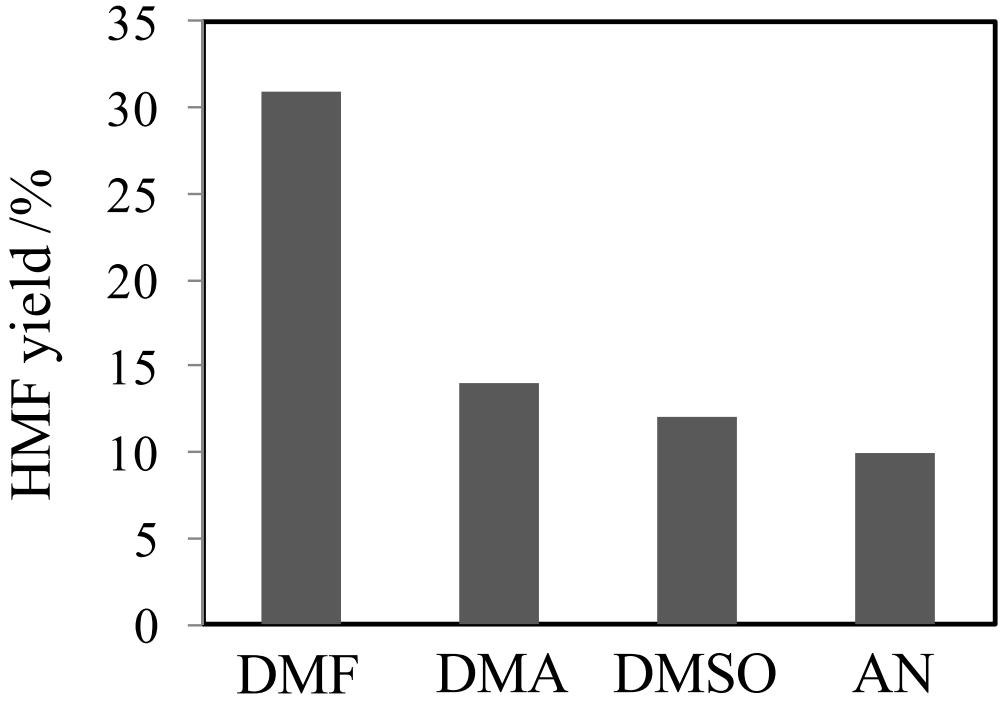

Fig. S3. Yields of 5-hydroxymethylfurfural (HMF) from glucose using hydrotalcite and Amberlyst-15 in polar aprotic solvents. Reaction conditions: glucose (0.1 g), hydrotalcite (0.2 g), Amberlyst-15 (0.1 g), solvent (3 mL), 373 K, 3 h. Solvent: *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO) and acetonitrile (AN).