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酸性离子液体催化纤维素在生物丁醇中转化为乙酰丙酸丁酯

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Conversion of Cellulose to Butyl Levulinate in Bio-Butanol Medium Catalyzed by Acidic Ionic Liquids

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The typical procedures for synthesis of SFILs: *N*-methylimidazole (8.21 g, 0.1 mol) and 1,4-butanesultone (13.64 g, 0.1 mol) were charged into a 50 mL round bottom flask and stirred at 50 ℃ for 20 h to get white zwitterionic-precursor 4-(3-methylimidazolium)butane sulfonate. After the precursor prepared was purified through washing with ether (3×20 mL), a stoichiometric amount of concentrated mineral acid (HCl, H_3PO_4 or H_2SO_4, 0.1 mol) was added dropwise. The mixture was reacting while stirred vigorously at 80 ℃ for 6 h. At last, the acidic ILs were obtained as colorless or yellowish viscous liquid after being washed with ether (3×20 mL) and then dried under vacuum at 80 ℃ for 24 h.

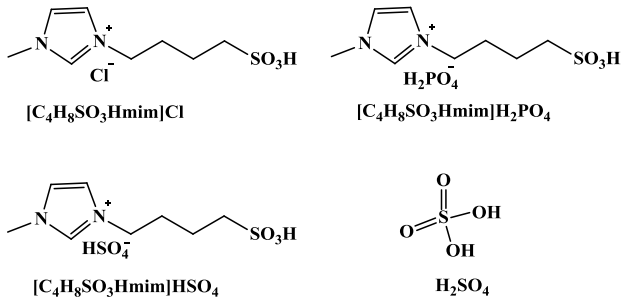


Fig.S1 Catalysts used in this study

[$C_4H_8SO_3$Hmim]Cl: ^{1}H NMR (400 MHz, D_2O): δ=8.66 (s, 1H); 7.42 (s, 1H); 7.36 (s, 1H); 4.17 (t, *J*=8 Hz, 2H); 3.82 (s, 3H); 2.87 (t, *J*=8 Hz, 2H); 1.91-1.99 (m, 2H); 1.63-1.71 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ=135.96; 123.64; 122.15; 50.03; 48.90; 35.64; 28.07; 20.90. ESI-MS: *m*/*z* (＋): 219.1; *m*/*z* (－): 35.4. Onset decomposition temperature: 338.9 ℃.

[$C_4H_8SO_3$Hmim]H_2PO_4: ^{1}H NMR (400 MHz, D_2O): δ=8.55 (s, 1H); 7.39 (s, 1H); 7.33 (s, 1H); 4.14 (t, *J*=8 Hz, 2H); 3.78 (s, 3H); 2.84 (t, *J*=8 Hz, 2H); 1.88-1.95 (m, 2H); 1.60-1.67 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ=135.91; 123.61; 122.12; 50.01; 48.87; 35.61; 28.04; 20.87. ESI-MS: *m*/*z* (＋): 219.3; *m*/*z* (－): 97.4. Onset decomposition temperature: 336.8 ℃.

[$C_4H_8SO_3$Hmim]HSO_4: ^{1}H NMR (400 MHz, D_2O): δ=8.63 (s, 1H); 7.40 (s, 1H); 7.34 (s, 1H); 4.15 (t, *J*=8 Hz, 2H); 3.79 (s, 3H); 2.85 (t, *J*=8 Hz, 2H); 1.89-1.96 (m, 2H); 1.60-1.68 (m, 2H). ^{13}C NMR (100 MHz, D_2O): δ=135.93; 123.63; 122.13; 50.02;

48.88; 35.62; 28.05; 20.88. ESI-MS: *m*/*z* (＋): 219.0; *m*/*z* (－): 97.1. Onset decomposition temperature: 327.7 ℃.

Table S1 Properties of the BuOH, BF, Dibutyl ether, and BL

Sample	Boiling point (℃)	Solubility in water (*w*, %)	Ref.
BuOH	118	7.3 (25 ℃)	1
BF	106	0.75 (27 ℃)[a]	2
Dibutyl ether	142	0.03 (25 ℃)	1
BL	232	1.3 (25 ℃)	3

[a] calculated from the data (0.75 g/100 mL) given in Pubchem database

Distribution of catalysts in BuOH and H_2O

The distribution of acidic catalyst in BuOH/H_2O biphasic system was determined by comparing the weight of catalyst distributed in each phase after stirring at 25 ℃.

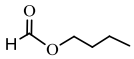
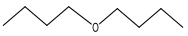
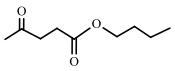
Table S2 Distribution of catalysts in BuOH/H_2O

Catalyst	Distribution[a] /%		Recovery (%)
	BuOH	H_2O	
$[C_4H_8SO_3Hmim]Cl$	4.8±0.13	95.2±0.13	>99
$[C_4H_8SO_3Hmim]H_2PO_4$	4.5±0.11	95.5±0.11	>99
$[C_4H_8SO_3Hmim]HSO_4$	3.9±0.15	96.1±0.15	>99
H_2SO_4	47.1±0.46	52.9±0.46	<75

[a] 0.5 mmol catalyst, 10 mL H_2O and 10 mL BuOH at 25 ℃

Table S3 BuOH soluble chemicals determined by GC-MS (Table 1, entry 4)

RT (min)	Compound[a]		Percentage (%)[b]
	Name	Structure	

3.07	butyl formate		11.45
5.51	dibutyl ether		48.94
8.82	butyl levulinate		39.61

[a] identified according to the NIST MS library; [b] measured using peak area normalization method

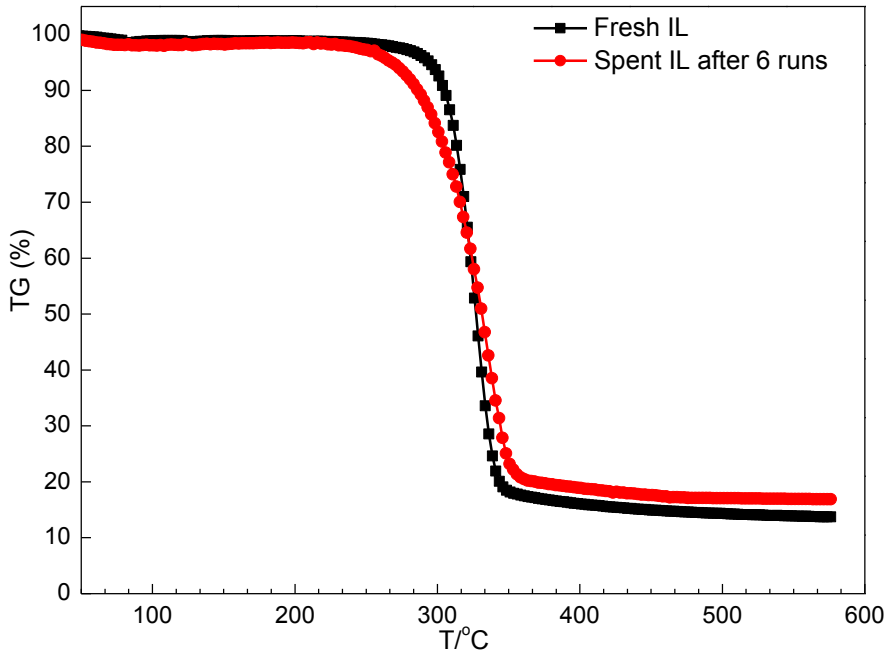


Fig.S2 TG curves of fresh IL and spent IL after 6 runs

Oven temperature: 50 to 550 ℃ at a rate of 10 ℃ min^{-1}

References

(1) Smallwood, I. *Handbook of Organic Solvent Properties*; Butterworth-Heinemann: London, 1996.

(2) http://pubchem.ncbi.nlm.nih.gov/compound/11614.

(3) Christensen, E.; Williams, A.; Paul, S.; Burton, S.; McCormick, R. L. *Energ. Fuel.* **2011,** *25* (11), 5422.