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Electronic Supplementary Information (ESI)

A Catalytic Aldol Condensation System Enables One Pot Conversion of Biomass Saccharides to Biofuel Intermediates

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1. General Methods

All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. Furfural (Sinopharm Chemical Reagent Co., Ltd, 99%); Acetone (Kermel, 99.5%); 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) (Lanzhou Greenchem ILs, 99%), $NiCl_2$ (Shanghai Chemical Reagent, 98%), $CoCl_2\cdot 6H_2O$(Aladdin, 96%), $CrCl_3\cdot 6H_2O$ (Aldrich, 96%), $CrCl_2$ (Alfa Aesar, 99.9%),VCl_3 (Alfa, 99%), $FeCl_3$ (Sinopharm Chemical Reagent Co., Ltd, 97%), $CuCl_2\cdot 2H_2O$ (Sinopharm Chemical Reagent Co., Ltd, 99%), Ethylene glycol dimethyl ether (GDE) (Sinopharm Chemical Reagent Co., Ltd, 99%), Ethanol (Sinopharm Chemical Reagent Co., Ltd, 99.7%), Methyl tert-butyl ether (MTBE) (Tian jin Guangfu Fine Chemical, 99%), Ethyl acetate (Kermel, 99.5%), Cyclohexanone (Sinopharm Chemical Reagent Co., Ltd, 99.5%), 4-(2-furyl)-3-buten-2-one (FA) (Energy, 98%), Methanol (Kermel, 99.5%), Isopropanol (Sinopharm Chemical Reagent Co., Ltd, 99.5%), N-proranol (Sinopharm Chemical Reagent Co., Ltd, 99%), N-butanol (Sinopharm Chemical Reagent Co., Ltd, 99.5%), Isobutanol, T-butanol (Kermel, 99.7%), 2-furaldehyde diethyl acetal (FDEA) (Energy，97%), Xylose (Sinopharm Chemical Reagent Co., Ltd, 99%). NaOH (Sinopharm Chemical Reagent Co., Ltd, 96%).

2. Experimental Section

The dehydration of [BMIM]Cl: Weigh specific amounts of fresh [BMIM]Cl in a round bottom flask; The material was heated at 100 ^{o}C for at least 5 h under vacuum. The flask was then filled with nitrogen and transferred to a glovebox in preparation for the experiments.

Furfural purification: Take specific amounts of furfural in a round bottom flask; Heated at 65 ^{o}C and pure furfural can be obtained by vacuum distillation.

1,5-bis-(2-furanyl)-1,4-pentadien-3-one (FAF) synthesis [1]: FAF was prepared by condensing FA with furfural. The reaction was carried out by mixing 2.1 g furfural, 3.0 g FA, 0.6 g NaOH pellets, 80 g water and 80 g methanol in a well-stirred glass reactor at room temperature for 10 h. The solution was then neutralized with HCl and the solvent was evaporated. The resulting solid product was washed with H_2O to remove NaCl.

For reaction experiments, Weight appropriate amounts of [BMIM]Cl and metal chloride in 20 mL thick-walled glass reactors and heated to make sure metal chloride was dissolved well in [BMIM]Cl under agitation using a magnetic stirrer bar in a glovebox filled with dry nitrogen. Cool them down and add specific amount of reactants. Take the glass reactor out from the glovebox and put it into a 50 mL stainless batch tank reactor with a pressure gage. And then inject nitrogen into the reactor to increase its pressure to 500 psi. The reactors were then placed on a magnetic heated stirrer at the desired reaction temperature and stirred at 500 rpm. Reactors were removed from the magnetic heated stirrer at specific reaction times and cooled by flowing cool water. After reaction, prepare a silica column filled with about 60 g SiO_2 (100-200 mesh). Then remove [BMIM]Cl through this column washing with about 80 mL ethyl acetate. Then the products and reactants were all dissolved in ethyl acetate. Remove most ethyl acetate with rotary evaporator and analyze them with GC-MS. Take several dominating fragment peaks to quantify the sample. And N, N- Dimethylformamide (DMF) acts as the internal standard.
After the reaction, pure 4-(2-furyl)-3-buten-2-one (FA) and 1,5-bis-(2-furanyl)-1,4-pentadien-3-one (FAF) were obtained [2, 3] through several columns washing with the combination of ethyl acetate and petroleum ether.
FA is a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50 (d, J = 1.44, 1H), 7.28 (d, J

= 15.92, 1H), 6.67 (d, *J* = 3.4, 1H), 6.62 (d, *J* = 15.96 Hz, 1H), 6.49 – 6.48 (m, 1H), 2.33 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 150.9, 145.0, 129.4, 124.3, 115.6, 112.5, 27.9.

FAF is a yellow solid.^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51 – 7.46 (m, 4H), 6.92 (d, *J* = 15.6 Hz, 2H), 6.69 (d, *J* = 3.4 Hz, 2H), 6.50 – 6.49 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 151.6, 144.9, 129.2, 123.2, 115.8, 112.6.

3. Supporting Graghs

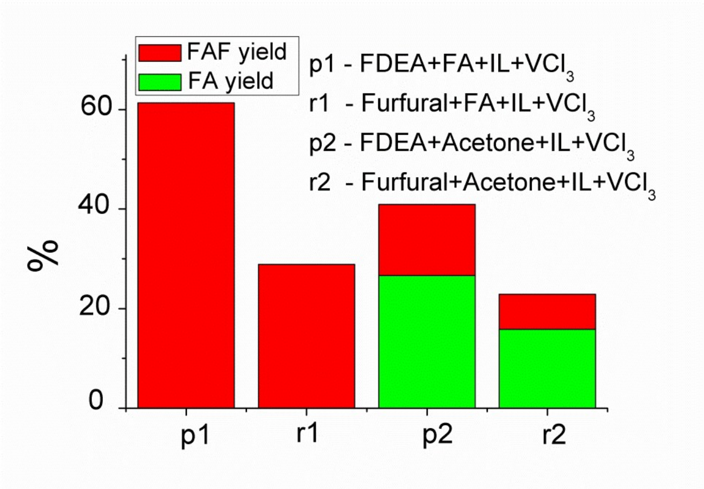

Fig. S1 The reactivity of p1 vs p2 and r1 vs r2. IL =[BMIM]Cl.

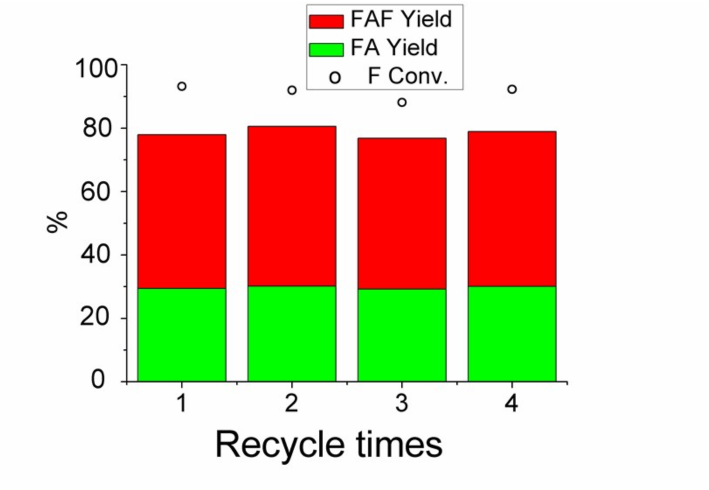

Fig. S2 Results of catalytic furfural condensation with acetone in the presence of ethanol using fresh and recycled catalytic system composed of VCl_3/[BMIM]Cl. Reaction conditions: Furfural 2.08 mmol, [BMIM]Cl 2 g, VCl_3, 0.13 mmol, Acetone 10.40 mmol, Ethanol 12.50 mmol; 140 °C. 5 h.

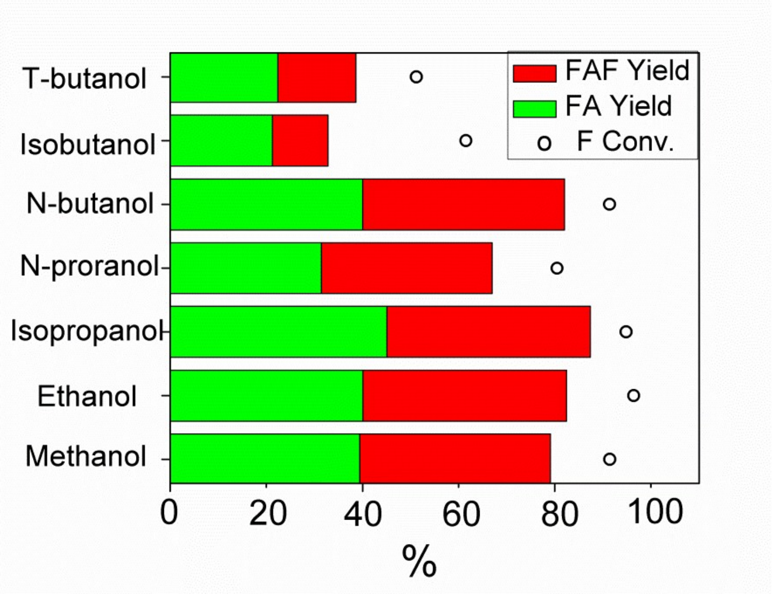

Fig. S3 The effect of selected alcohols on furfural condensation with acetone catalyzed by VCl_3 in [BMIM]Cl. Reaction conditions: Furfural 2.1 mmol, [BMIM]Cl 2.00 g, VCl_3, 0.13 mmol, Acetone 10.4 mmol, Alcohol 20.8 mmol; 140 °C. 1.5h.

We further studied the effect of several alcohols on furfural condensation with acetone. The addition of all straight-chain alcohols (C1-C4) showed better promotional results than branched chain alcohols (C1-C4) (Fig. S3). Although all these alcohols reacted with furfural to form acetals detected by GC-MS, the acetals with branched chain alcohol may pose the steric hindrance effect for the condensation so their reactivity with acetone was decreased. The reduced reactivity due to the branched alcohol is evidenced by the lower conversion (Fig. S3). As a result, branched chain alcohols (C1-C4) displayed rather poor catalytic results.

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