Electronic Supplementary Material (ESI) for Green Chemistry.

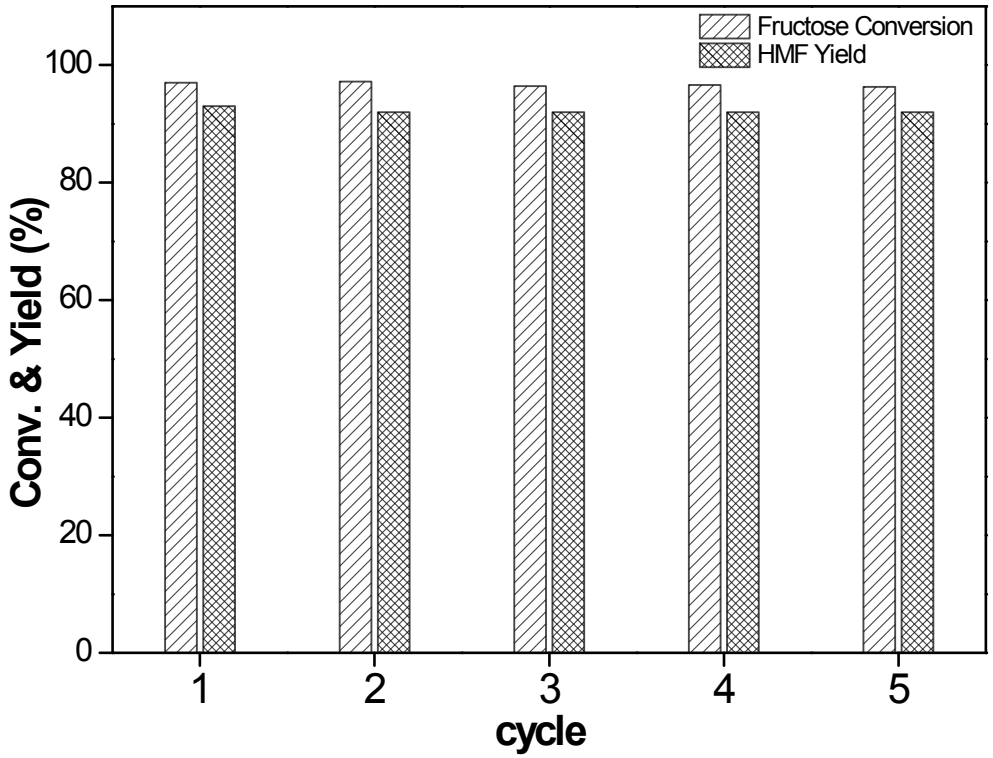

Figure S1. Reusability of Amberlyst-15 catalyst for fructose dehydration to HMF

Reaction conditions: Amberlyst-15 1.0 g, Fructose 15 g, BuOH 85g, 100 °C, reaction time 5h, 1000 rpm

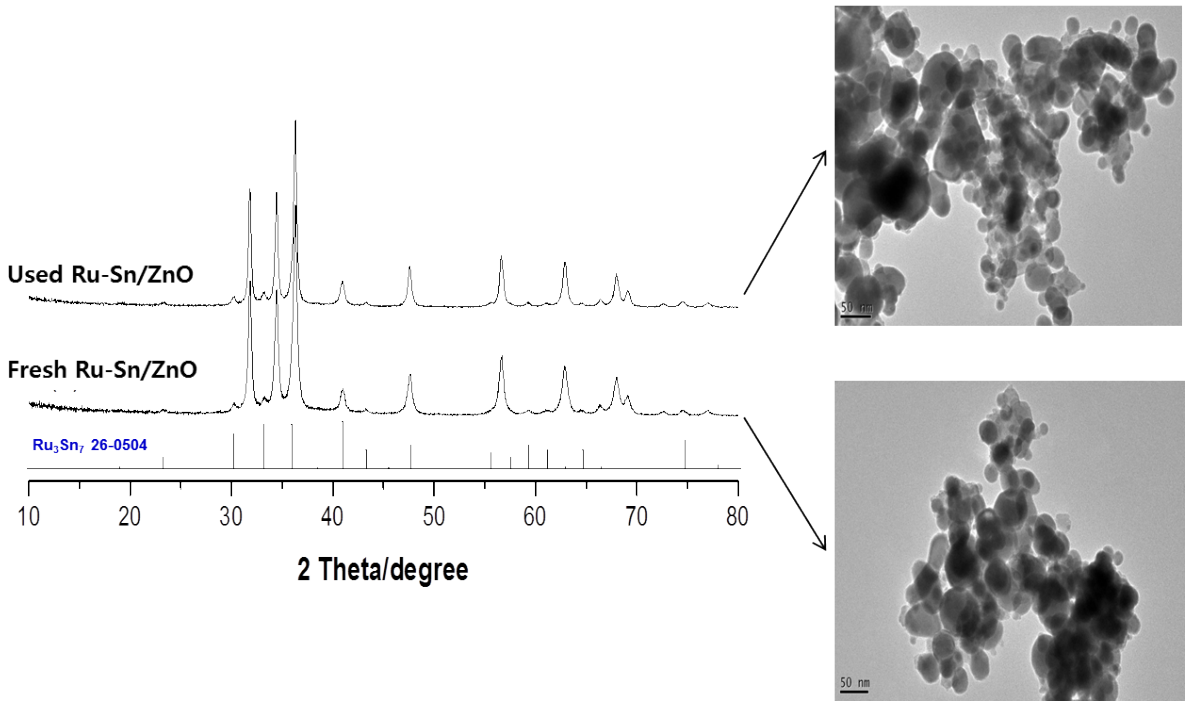

Figure S2. XRD and TEM of Ru-Sn/ZnO before and after 300 h of reaction

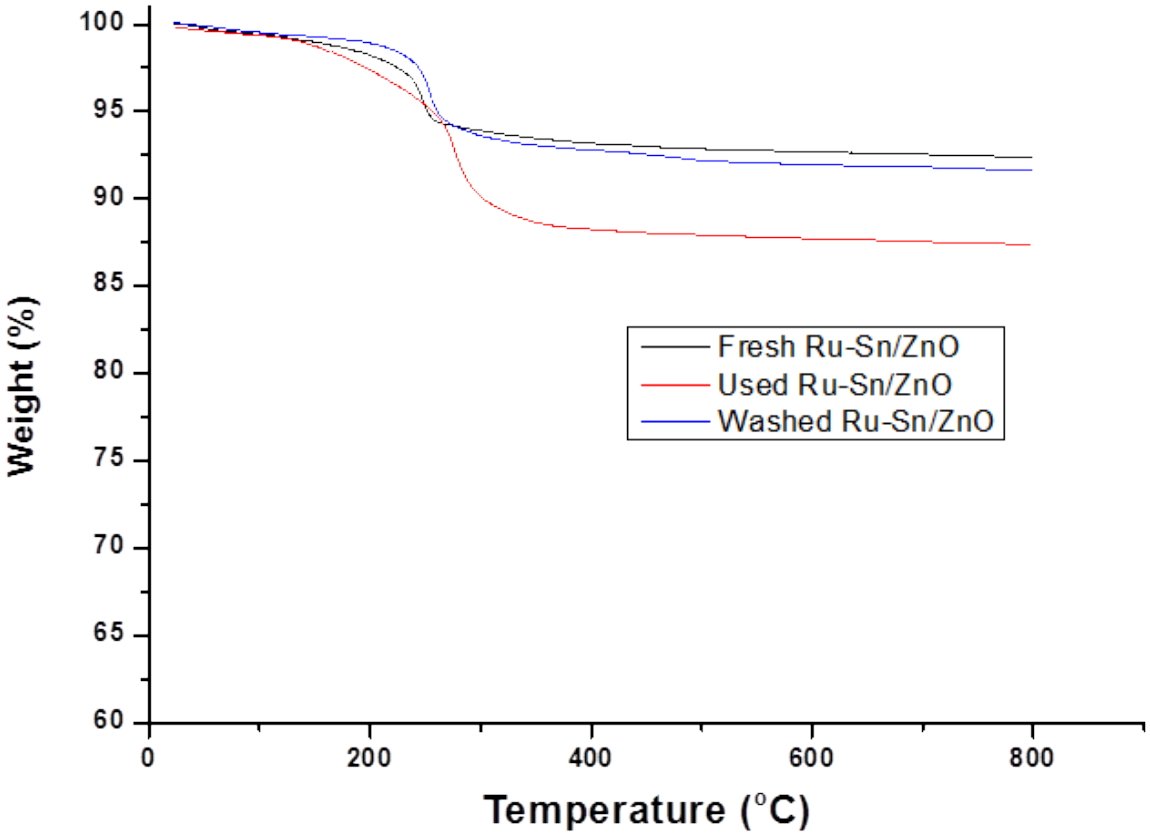

Figure S3. TGA of Ru-Sn/ZnO before and after 300 h of reaction

1. Materials

D-Fructose (99%, ACROS Organics),5-hydroxymethylfurfural (HMF, 99.9%, Sigma Aldrich), D-cellubiose (99%, Sigma Aldrich), Amberlyst-15(Sigma Aldrich), 1-butanol (BuOH, 99.9%, Acros Organic), $RuCl_3.xH_2O$ (99.9%, Stream Chemicals), $SnCl_4.5H_2O$ (98.0%, Kanto Chemicals), $Zn(NO_3).6H_2O$ (99%, Acros Organic) and NaOH (Samchun Chemical), tetrahydrofuran (99.5%, Samchun Chemical), dimethylsulfoxide (99%, Sigma Aldrich), γ-valerolactone (99.9%, Sigma Aldrich), 5-methylfuran (99.9%, Sigma Aldrich), 5-methlfurfuralalcohol, 2, 5-dihydroxmethylfrufural (99.9%, Sigma Aldrich), and H_2SO_4 (98%, Samchun chemicals) were used without further purification.

2. Ru-Sn/ZnO catalyst preparation

Ru–Sn/ZnO catalysts with 1.4 wt% Ru and a Ru/Sn molar ratio of 0.5 were prepared by sequential coprecipitation–deposition using aqueous solutions of $Zn(NO_3)_2.6H_2O$, $SnCl_4.5H_2O$, and $RuCl_3.xH_2O$ at pH 7.2–7.5. Typically, an aqueous solution of 0.1 M $Zn(NO_3)_2.6H_2O$ and 1.0 M $SnCl_4.5H_2O$ were simultaneously added dropwise into 200 ml water and the pH was adjusted to 7.5 via dropwise addition of NaOH. After precipitation, the solution was stirred for 12 h at room temperature and then 0.5 M RuCl3·xH2O solution was added dropwise and the pH of the solution was maintained at 7.2 by continuous addition of NaOH. The solution was stirred for 5 h at room temperature and left to sit at 85°C for 5 h. The solution was then filtered and washed with distilled water until the filtrate was free from sodium and chloride ions. The resultant solid was dried at 120 ^oC in air for 12 h, pressed, crushed, and sieved (size 320–420 μm). The catalysts were reduced by direct reduction without calcination at 420 ^oC for 6 h.

3. Fructose dehydration

The fructose dehydration was carried out in a round bottom flask equipped with reflux condenser and temperature controllable magnetic stirrer. In a typical experiment, 15g of fructose and 1.0 g of Amberlyst-15 were added to BuOH. It should be noted that 15wt% fructose has limited solubility in BuOH at room temperature, but it is completely soluble at 100 ^oC. The dehydration reaction was carried out at 100 ^oC with stirring at 1000 rpm for 5 h of reaction time. The reaction mixture was then cooled down to room temperature. The unreacted fructose and catalyst were separated by simple filtration from the HMF/BuOH

mixture. The used catalyst was also easily separated from fructose by washing with water, and then it was used for the next cycle experiment after drying at 100 ^{o}C. To obtain HMF with higher purity, the crude HMF was further purified by washing with 1M NaCl solution to extract the dissolved fructose and humin impurities into the aqueous phase. The concentration of HMF and fructose was analyzed by HPLC (Youngin HPLC, Korea) equipped with refractive index detector and Bio-Rad Aminex® HPX-87H (300 mm x 7.8 mm) column using 0.05 M H_2SO_4 as a mobile phase.

4. DMF production from HMF

Continuous catalytic measurements were performed in a fixed-bed down-flow stainless steel (SUS 316) reactor under atmospheric pressure. 1.0 g of pelletized Ru-Sn/ZnO was placed in the middle of the reactor on SUS support. In order to vaporize HMF/BuOH mixture, the reaction condition was maintained at 240 ^{o}C, 1 atm, and 20 mL/min H2 flow by changing the weight hourly space velocity of the HMF feed.

In a batch-type reaction system, HMF 12 w% in BuOH 100 g along with 1.0 g of pelletized Ru-Sn/ZnO was introduced into a 200 ml autoclave reactor. After increasing the reaction pressure to 10 bar of H_2, the reaction was carried out at 180 ^{o}C and 800 rpm for 2h. The reactor was the cooled down and the catalyst was removed by simple filtration.

The product selectivity was analyzed by gas chromatography equipped with a cyclosil-B column (30 m X 0.32mm X 0.25um) and FID detector. HMF conversion was analyzed by HPLC (Youngin HPLC, Korea) equipped with a refractive index detector and Bio-Rad Aminex® HPX-87H (300 mm x 7.8 mm) column using 0.05 M H_2SO_4 as a mobile phase.