Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Materials

Valorization of poly(butylene succinate) to Tetrahydrofuran *via* one-pot catalytic hydrogenolysis

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1. Experimental details

1.1 Visualization reaction

The tests were conducted in a 50 ml autoclave reactor with a transparent glass made of sapphire (SenLong Experimental Apparatus Co. Ltd., China). 1.5 g PBS and 0.15 g of Pd/C catalyst were mixed and loaded in the autoclave reactor. The reactor was: (1) sealed and flushed with H_2 three times, (2) pressurized with H_2 to 3.0 MPa at room temperature, and (3) heated up to the given temperature (i.e., 240 ^{o}C) in ~70 min and then hold for 36 h.

1.2 Catalytic hydrogenation of succinic acid/ butanediol/ gamma-butyrolactone/succinic anhydride

The catalytic hydrogenation was performed in a 100 ml autoclave reactor with a mechanical stirrer and an electric temperature controller. Given amount of reactants, i.e. 5.9 g of succinic acid, or 4.5 g of butanediol, or 4.3 g of gamma-butyrolactone, or 5.0 g succinic anhydride, was added into the reactor. The reactor was: (1) loaded with catalysts (mass ratio of catalyst: PBS=1:10) and purged with H_2 three times, (2) pressurized with H_2 to 6.0 MPa at room temperature, and (3) heated up to the given temperature (i.e., 240 ^{o}C) in ~70 min and then hold for 24 h.

1.3 Catalytic hydrogenolysis over other catalysts

Two types of Cu/Zn/Al catalysts (with mass ratios of 55:35:10 and 65:25:10, purchased from Sinopec Research Institute of Nanhua group, Nanjing, China) and Ru/C (containing 50 wt% H_2O, Macklin Reagent, Shanghai, China) were also employed for the hydrogenolysis reaction. All the tests were conducted in a 100 ml autoclave reactor. The reaction was performed with 8.4 g PBS and 0.84 g catalysts under 6.0 MPa H_2 pressure. The reactor was heating to the targeted temperature (i.e., 240 ^{o}C) in ~70 min and then hold for 36 h.

1.4 Catalytic hydrogenolysis in water solution

A given amount of deionized water was added into the 100 ml autoclave reactor as a solvent with 4.3 g PBS and 0.43 g Pd/C catalyst. The reactor was flushed with H_2 three times and then pressurized with H_2 to 6.0 MPa at room temperature. The reactants were heated to 240 ^{o}C in ~70 min and then hold for 12 h with a stirring rate of 500 r/min.

1.5 Liquid products analysis

The liquid products were qualitatively analyzed using a gas chromatograph-mass spectrometer (GC-MS, Shimadzu, QP2020, Japan) with two capillary columns (DB-5MS or Rtx-5MS). The optimized chromatographic conditions were injector temperature of 280 °C, ion source temperature of 200 °C, interface temperature of 285°C with helium as the carrier gas. The oven temperature program was set at 40°C (2 min) – (10°C /min) – 280 °C (2 min). Quantitative analysis of the liquid products from hydrogenation was performed using a GC instrument equipped with a flame ionization detector (FID, Shimadzu, 2014C) and a WondaCap-FFAP column, with an internal standard method (lactic acid was used as internal standard). After the reaction, pre-weighed lactic acid was added into the reactor at room temperature and mixed homogeneously with the liquid products. The column temperature was increased from 40 °C (with 3 min holding-time) to 240 °C at a heating rate of 10°C/min, using N_2 as the carrier gas. The injector and detector temperatures are 260 °C and 280 °C, respectively.

1.6 Gas analysis

After the reactor cooled down to room temperature, the pressure and volume of the gas products in the reactor were measured to calculate the total amount of the gas products formed. The amounts of alkanes, CO_2, and H_2 were quantitatively determined using a multi-dimensional gas chromatography (Kechuang, GC2002, China) with a thermal conductivity detector (TCD).

1.7 Pyrolysis-GC-MS (Py-GC-MS) analysis

0.5 g PBS sample was placed in the sample cup and felt into the pyrolyzer furnace (Frontier Laboratories Ltd, Fukushima, Japan). The pyrolysis temperature was set at 220 °C, and the GC oven temperature was programmed from 50 to 280 °C with a heating rate of 20 °C/min. The volatile organic compounds were separated in an Ultra-Alloy metal capillary column (UA+5) and analyzed by an MS detector (Shimadzu QP2010 Ultra, Japan).

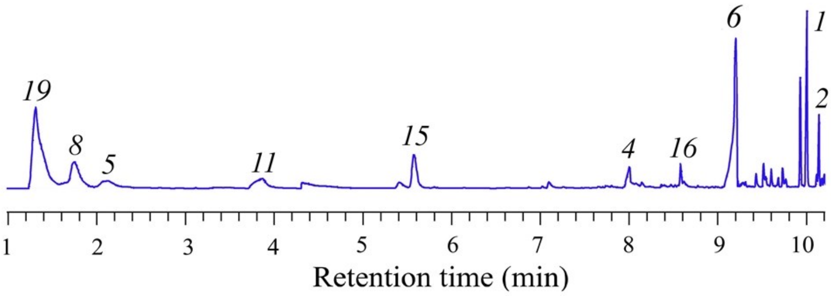

Figure S1. Py-GC-MS analysis of liquids from PBS pyrolysis at 220 ^{o}C under N_2 atmosphere: (1) butane succinate, (2) butylene succinate, (4) butanediol, (5) butenol, (6) succinic anhydride, (8) tetrahydrofuran, (11) propionic acid, (15) butyl propionate, (16) propyl propionate, (19) 1,3 butadiene.

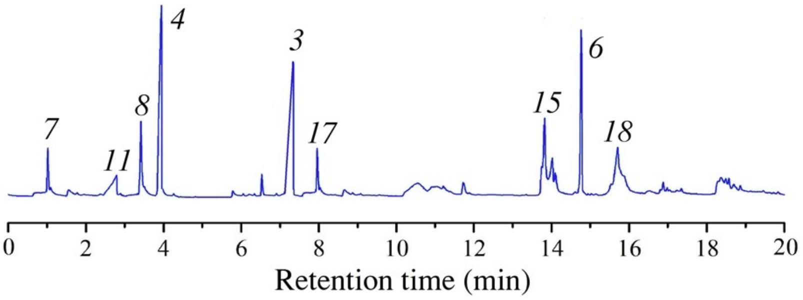

Figure S2. GC-MS analysis of oil products from catalyst-free pyrolysis of PBS under H_2 atmosphere (reaction at 240 ^{o}C for 12 h): (3) succinic acid, (4) butanediol, (6) succinic anhydride, (7) gamma-butyrolactone, (8) tetrahydrofuran, (11) propionic acid, (15) propyl propionate, (17) propyl butyrate, (18) butyl butyrate.

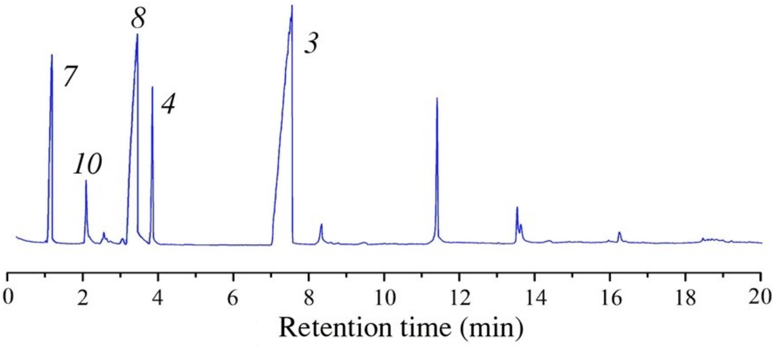

Figure S3. GC-MS analysis of oil products from catalyst-free hydrolysis of PBS at 240 ^{o}C for 12 h with 5% water dosage under H_2 atmosphere: (3) succinic acid, (4) butanediol, (7) gamma-butyrolactone, (8) tetrahydrofuran, (10) butanol.

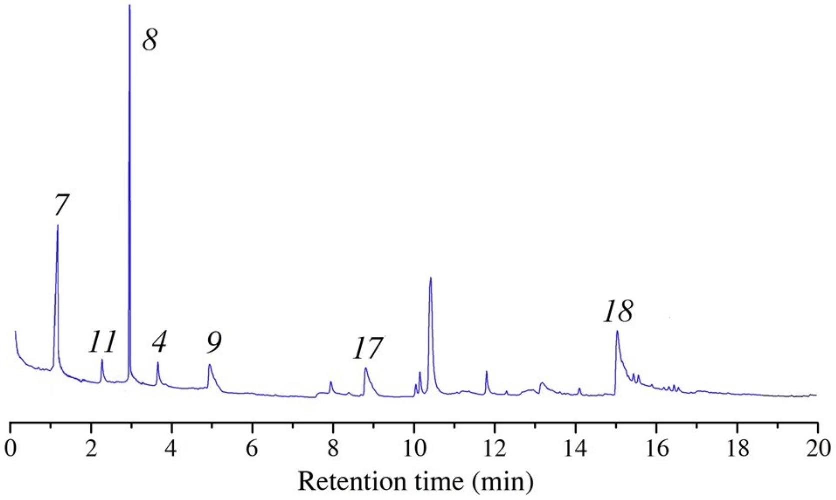

Figure S4. GC-MS analysis of oil products from catalytic hydrogenolysis of SA over Pd/C at 240 °C for 24 h: (4) butanediol, (7) gamma-butyrolactone, (8) tetrabydrofuran, (9) butyric acid, (11) propionic acid, (17) propyl butyrate, (18) butyl butanoate.

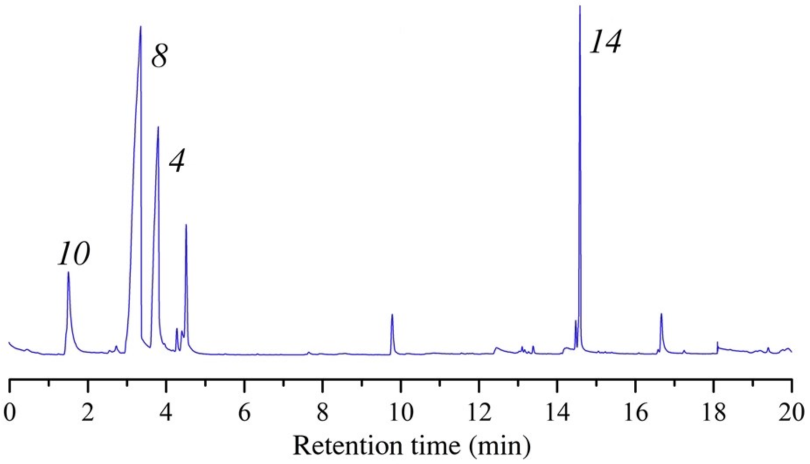

Figure S5. GC-MS analysis of oil products from catalytic hydrogenolysis of BDO over Pd/C at 240 ^{o}C for 24 h: (4) butanediol, (8) tetrabydrofuran, (10) butanol, (14) n-butyl ether.

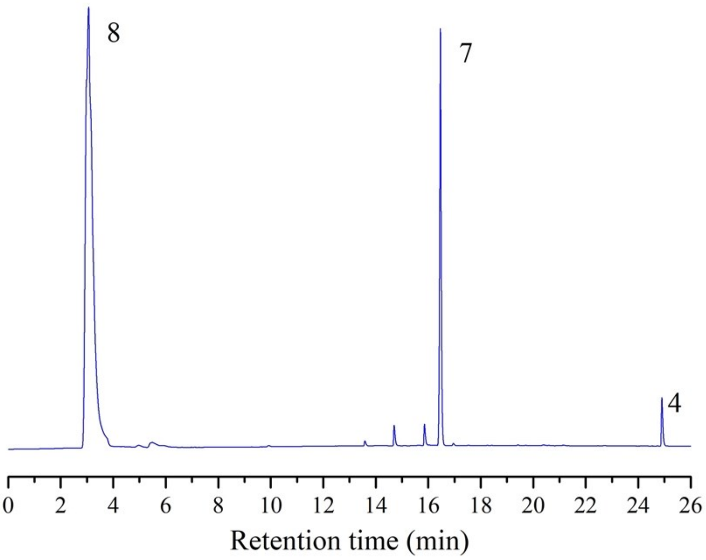

Figure S6. GC-FID analysis of oil products from catalytic hydrogenolysis of SAH over Pd/C at 240 ^{o}C for 24 h: (4) butanediol, (7) gamma-butyrolactone, (8) tetrabydrofuran.

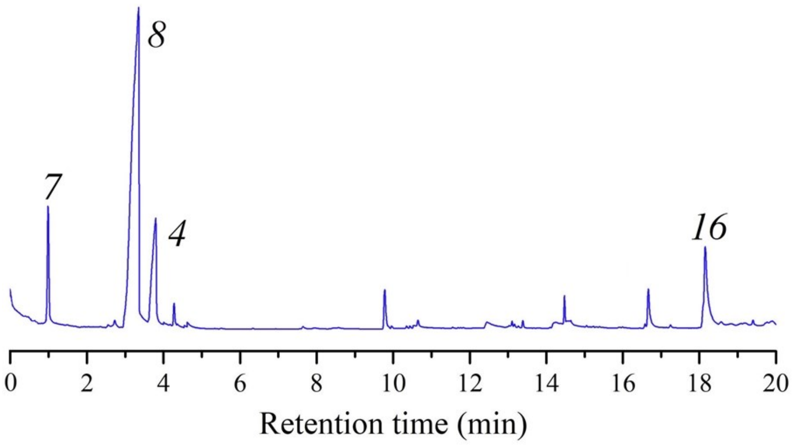

Figure S7. GC-MS analysis of oil products from catalytic hydrogenolysis of GBL over Pd/C at 240 ^{o}C for 24 h: (4) butanediol, (7) gamma-butyrolactone, (8) tetrabydrofuran, (16) propyl proionate.

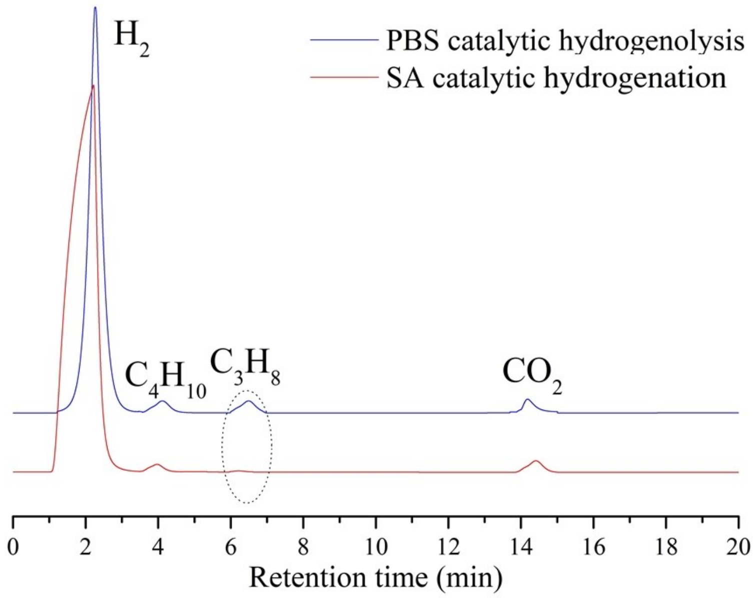

Figure S8. GC-TCD analysis of gases from hydrogenolysis of PBS and SA over Pd/C under 240 ^{o}C for 12 h.