

Biobased Catalyst for biorefinery processes: Sulphonated Hydrothermal Carbon as Catalyst for Glycerol Esterification

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Experimental procedures

Materials

Deloxan ASP I/9 (propylsulfonic polysiloxane, 0.1-0.4 mm particle size) was a gift from Degussa. Dowex CCR-2 (carboxylic polyacrylic resin, 20-50 mesh), and Dowex 50W×2 (sulfonic gel-type polystyrene resin, 2% divinylbenzene) were purchased from Fluka. Amberlyst 15 (sulfonic macroreticular polystyrene resin, 20% divinylbenzene) was purchased from Alfa Aesar. Glycerol was purchased from Fluka, glacial acetic acid from Scharlau and butyric and octanoic acids were purchased from Aldrich.

Catalyst preparation

Hydrothermal synthesis was carried out from D-glucose (25 mL, 1M in water) as previously described.^[1] The resulting material was then treated with concentrated (>96%) sulfuric acid (20 mL H₂SO₄/g solid) under argon atmosphere at 150°C for 15h. The sulfonated samples were then thoroughly washed with hot distilled water (about 3L of water per gram of catalyst) until neutral pH of the filtrate, and dried overnight at 105°C.

Catalyst characterization^[2]

CHS analyses were carried out by combustion in a ThermoFlash 1112 elemental analyzer equipped with a TCD detector.

Oxygen analysis was done by direct assay, which involves pyrolysis of the sample. Surface areas were determined by N₂ adsorption at 77 K (BET) using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 423 K. Alternatively it was also determined by CO₂ adsorption (Dubinin-Radushkevich) at 273 K in the same apparatus, after outgassing under the same conditions.

The total amount of acid sites on each catalyst was determined by back titration. The solid (50 mg) was added to 25 mL of 0.01M NaOH solution and allowed to equilibrate under stirring for 1 h. Thereafter, it was titrated with 0.05M potassium hydrogen phthalate solution using a Crison pH Burette 24.

NMR spectra were recorded in a Bruker Avance III WB400 spectrometer with 4 mm zirconia rotors spun at magic angle in N₂ at 10 kHz. ¹H–¹³C CP (cross-polarization) spectra (up to 10000 scans) were measured using a ¹H $\pi/2$ pulse length of 2.45 μ s, with a contact time of 2 ms, and spinal64 proton decoupling sequence of 4.6 μ s pulse length. Acid strength was determined by ³¹P MAS NMR spectra of adsorbed triethylphosphine oxide (TEPO) using a ³¹P $\pi/2$ pulse length of 4.3 μ s, without proton decoupling, with 30 s recycle delay.

[1] J. M. Fraile, E. García-Bordejé, L. Roldán, *J. Catal.* **2012**, 289, 73–79.

[2] J. M. Fraile, E. García-Bordejé, E. Pires, L. Roldán, *Carbon* **2014**, 77, 1157–1167.