processes

MDPI

Supplementary Materials

An Expedient Catalytic Process to Obtain Solketal from Bi-obased Glycerol

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Glassware

In order to prepare solketal (**1**) on bigger scale (100 g) a standard Dean-Stark trap was modified by the simple introduction of a long arm funnel. Figure S1 depicts the working apparatous.

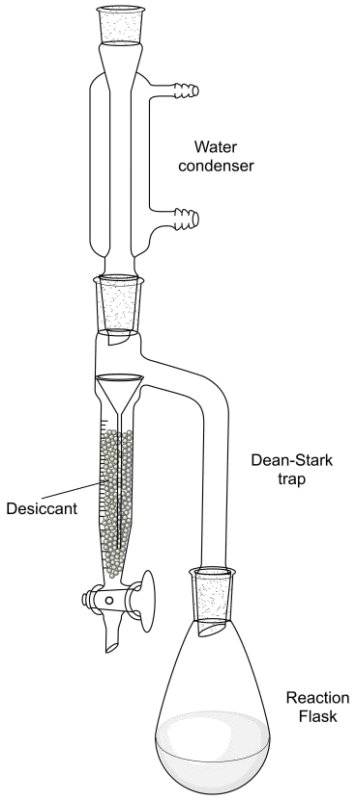

Figure S1. Modified glassware for continuous solvent drying

^{1}H-NMR Spectra of the Product

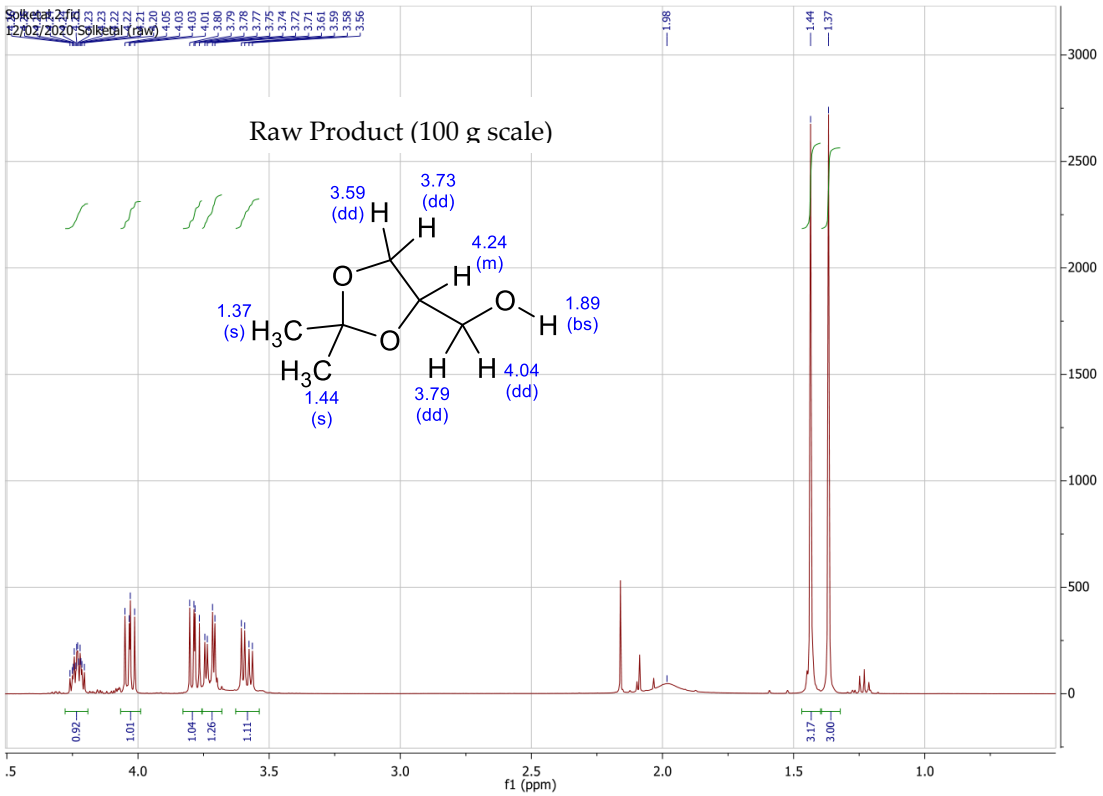

Figure S2. Crude solketal (**1**) ^{1}H NMR spectra (100 g scale)

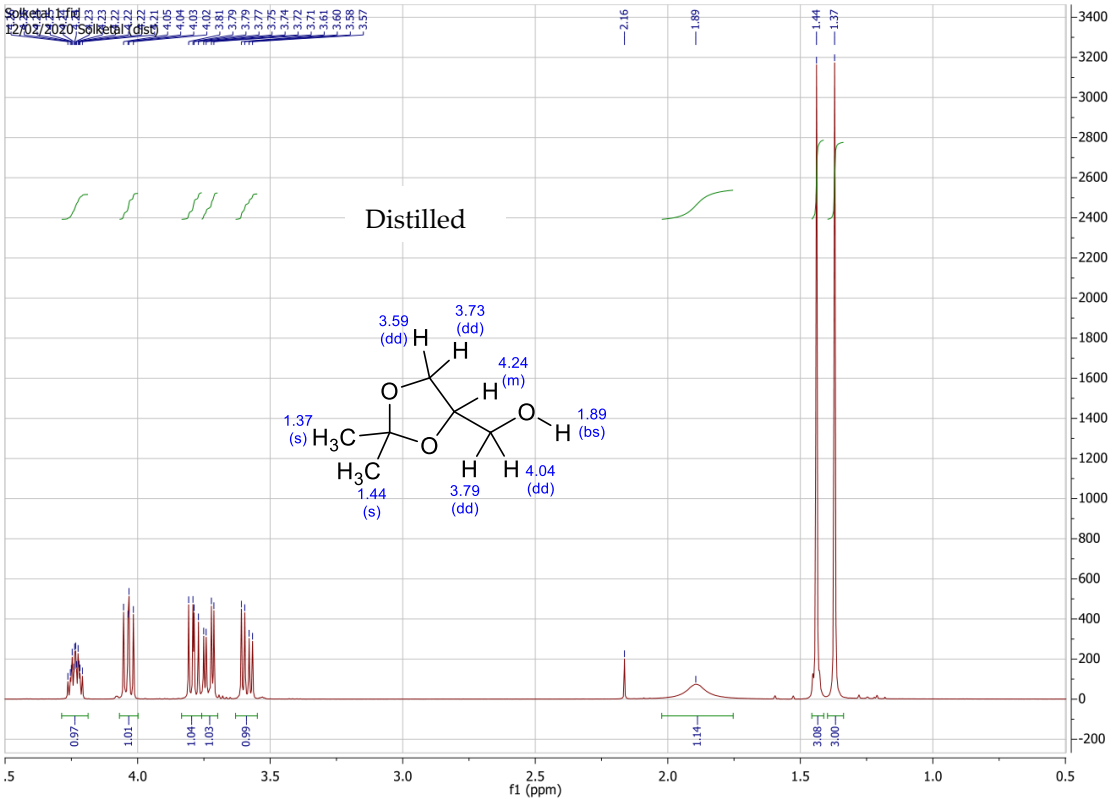

Figure S3. Distilled solketal (**1**) ^{1}H NMR spectra

Catalyst regeneration (100 g **gly** scale)

5.5 g of SSANa (3.0 mmol/g) containing 16.5 mmol $NaHSO_4$, prepared as described in section 2.2, were used in a first acetalization, involving 100 g of **gly**. Filtration at the end of the process let the recovery of a white-yellowish powder, that was subjected to thermal regeneration (600 °C, overnight). The resulting white powder (4.75 g, composed of 3.52 g of SiO_2 and around 8.25 mmol of Na_2SO_4) was transferred in a 25 mL round bottom flask and 8.25 mmol of H_2SO_4 (6.9 mL of an 1.2 M aqueous solution) were added. The suspension was stirred for one hour. Once evaporated to dryness at the rotavapor, the solid residue (free-flowing powder) was oven-dried at 130 °C overnight, giving the regenerated SSANa (3.0 mmol/g) as white powder (5.5 g).

The following scheme (Figure S4) describe the fate of bisulfate during thermal treatment - regeneration of the catalyst. First a molecule of water was lost (around 315 °C), forming pyrosulfate ($Na_2S_2O_7$). This, around 460°C, loses half of the sulfur as SO_3, giving sodium sulfate (Na_2SO_4). The reaction of this last with sulfuric acid let the re-formation of the bisulfate, through an acid-base process.

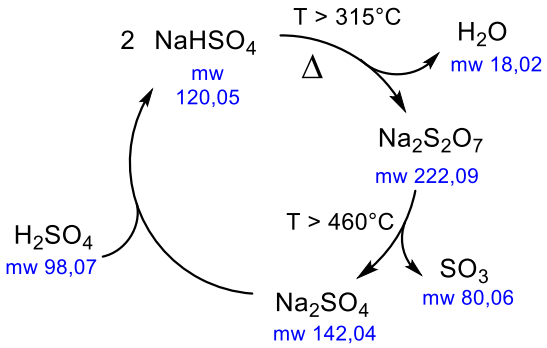

Figure S4. Catalyst regeneration cycle

Regenerated SSANa (3.0 mmol/g) retain high catalytic activity during the first five repetitions, as shown in Figure S5.

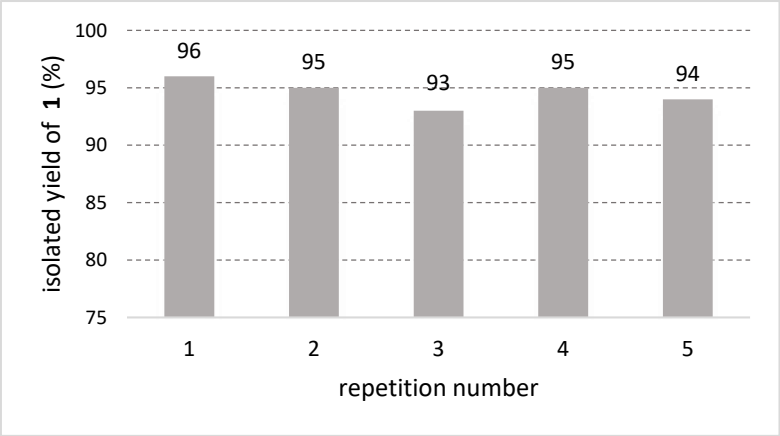

Figure S5. Performance of regenerated catalyst