Electronic supplementary information

Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts

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1. Materials

Sigmacell microcrystalline cellulose (5 wt% moisture, average size 20 µm, Sigma-Aldrich), sulfuric acid (Sigma-Aldrich, 0.5 M), Silica-Alumina (Davicat), Nafion SAC-13 (Sigma-Aldrich), Nb_2O_5 (CBMM), propylsulfonic silica functionalized (Silicycle), and Tosic (Silicycle) were used as received. Mordenite (Zeolyst) and ZSM-5 (Zeolyst) were calcined in air for 3 h at 723 K. Amberlyst 70 was rinsed prior to use with distilled water until the pH of the effluent solution stabilized and showed no indication of residual acidity, crushed, and dried overnight at 393 K.

1.1. Sulfonated Carbon

20 g of D-glucose (>99.5 %, Sigma) was pyrolyzed for 15 h at 673 K under Argon flow. The solid obtained was ground and stirred in 200 mL of fuming sulfuric acid (20% free SO_3, Aldrich) at 423 K for another 15 h. Finally, the mixture was diluted in 1 L of water, filtered, washed with distillated water until sulfuric acid was not detected in the effluent water, and dried in air at 373 K. This catalyst has been denoted as C-SO_3H in Table 1 in the main text.

2. Methods

2.1. Batch reactors

In a typical experiment, microcrystalline cellulose or dry corn stover (obtained through the Great Lakes Bioenergy Research Center (GLBRC) was added to a 10 mL thick-walled glass reactor to achieve a final cellulose concentration of 2 wt%. GVL and SA solution were added to obtain the appropriate SA concentration and GVL/water ratio. The reactor was immersed in an oil bath at 433 K and held for the indicated time. The reactor was then cooled to room temperature, and 0.1 g of sample was diluted to 1 mL using distilled water, syringe filtered (0.2 µm membrane), and analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column). If additional batches of biomass were added, no sample was taken between batches. The reactor was weighed, and another dose of solids (equal to the first addition) was added. The vessel was resealed, and a second or third cycle started. Samples were then taken using the procedure outlined above.

2.2.Flow reactor

Hydrogenation of LA made from cellulose, in presence of GVL, was carried out in a flow reactor operating in an up-flow configuration. The reactor (stainless steel 6.35 mm OD) was loaded with $RuSn_4/C^1$ catalyst held between two end plugs of silica granules and quartz wool. The catalyst was reduced in-situ for 2 h at 773 K (1 K min^{-1}) before use. The tubular reactor was fitted inside of an aluminum block and placed within an insulated furnace (Applied Test Systems). Bed temperature was monitored at the reactor wall using a Type K thermocouple (Omega) and controlled using a 16A series programmable temperature controller (Love Controls). The tubular reactor was heated using a heating tape (OMEGA) and insulated with glass wool tape. The feed to the flow reactor system was introduced into the reactor using an HPLC pump (Lab Alliance, Series I). The flow of H_2 during reaction (25 cm^3(STP) min^{-1}) was controlled by a mass flow controller (Brooks Instruments, 5850S). Reactor pressure (35 bar of H_2) was controlled using a back pressure regulator (GO BP-60). The reactor effluent flowed into a vapor-liquid separator wherein the liquid product was collected. Liquid samples were analyzed using an HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector). Identification of products was achieved using GC-MS analysis (Shimadzu GCQP-2010).

The feed was prepared using a Parr reactor. Microcrystalline cellulose (2 wt%), a solution of GVL/water (90 wt% GVL/10wt% water), and Amberlyst 70 (6 wt%) were added to a 450 mL reactor, then purged with Ar gas three times and heated to 443 K (9 K min^{-1} ramp) with a high-temperature fabric heating mantle. The reactor was maintained at 443 K for 16 h while stirring at approximately 600 rpm. At the end of the reaction time, the heating mantle was removed, and the built-in cooling line cooled the reactor to room temperature. At this point, the reactor was opened, and a new dose of microcrystalline cellulose (2 wt%) was added. The reactor was heated again to 443 K and held for 16 h. A total of 3 doses of cellulose were added.

2.3.Catalyst reutilization

Catalyst reutilization experiments were carried out in a system as described in 2.1. At the end of the reaction, the reactor was centrifuged separating the liquid from the catalyst. After removing this liquid, water was added to the reactor, and the reactor was stirred and centrifuged, followed by the removal of water. This process using water was repeated three times. Subsequently, this process was repeated using methanol, and finally, the catalyst was dried overnight at 323 K under vacuum.

2.4.Catalyst regeneration

To regenerate the catalyst, a 28.5 wt% H_2O_2 solution was added to the reutilized catalyst and stirred overnight at room temperature. The catalyst was then washed with water three times and methanol one time, centrifuging between washes to separate the liquid from the catalyst. Finally, the catalyst was dried overnight at 323 K under vacuum.

3. References

[1] S. G. Wettstein, J. Q. Bond, D. M. Alonso, H. N. Pham, A. K. Datye and J. A. Dumesic, *Appl. Catal. B-Environ.*, 2012, 117–118, 321-329