Supplementary information for

Liquid-Phase Catalytic Transfer Hydrogenation and Cyclization of Levulinic Acid and its Esters to γ-valerolactone Over Metal Oxide Catalysts

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Table S1. Catalytic transfer hydrogenation of ethyl levulinate over ZrO_2 in the presence of sec-butyl phenol with varying molar ratios of isopropanol to ester.[a]

Entry	**EL (wt%)**	**SBP (wt%)**	**Molar ratio IPA:EL**	**Time (h)**	**Conv (%)**	**GVL yield (%)**	**GVL formation rate (μmol g^{-1} min^{-1})**
1	9.6	86.4	1:1	16	28.0	18.1	2.2
2	8.6	77.1	4:1	16	77.3	72.6	--
3	7.7	69.7	7:1	1	34.5	33.4	70.1
4	7.7	69.7	7:1	16	97.3	93.3	--

[a] Batch reactions, mass ratio ZrO_2:EL = 1:2.4, 150 °C, 300 psig He. Only by-product detected was isopropyl levulinate.

Methods and Materials

Catalyst preparation

The γ-Al_2O_3 catalyst was used as-received (STREM, >97%, low soda). The MgO/Al_2O_3 catalyst was obtained by calcination of hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$, Aldrich) in 60 cc (STP)/min flowing air at 723 K for 4 h prior to use in batch experiments. The $CeZrO_x$ and ZrO_2 catalysts were prepared by precipitation of $Ce(NO_3)_3\cdot 6H_2O$ and $ZrO(NO_3)_2$ with NH_4OH (Aldrich), according to Serrano-Ruiz et al.[1] Solids were calcined in 60 cc (STP)/min flowing air at 723 K for 4 h prior to use in batch experiments. The MgO/ZrO_2 catalyst was prepared by precipitation of $Mg(NO_3)_2\cdot 6H_2O$ and $ZrOCl_2\cdot 6H_2O$ with NaOH (Aldrich), according to Aramendia et al.[2] Solids were calcined in 60 cc (STP)/min flowing air at 873 K for 4 h prior to use in batch experiments.

Batch reactor studies

Reactions were carried out using a 50 mL pressure vessel (Hastelloy C-276, Model 4792, Parr Instrument). After loading the reactant solution, catalyst, and magnetic stirrer bar into the reactor, the vessel was sealed, purged with 300 psig He, and pressurized with He (300 psig) to maintain the reaction mixture in the liquid phase. Mechanical stirring was maintained using a magnetic stirrer plate (500 rpm).

Continuous flow reaction experiments

The flow reactor was a 6.4 mm (0.25 inch) outer diameter stainless steel tube with wall thickness of 0.7 mm (0.028 inch). The catalyst bed consisted of calcined catalyst (0.25 g) loaded between a quartz wool plug and fused SiO_2 granules (-4+16 mesh, Sigma-Aldrich). The reactor was heated with a furnace composed of close-fitting aluminum blocks externally heated by an insulated furnace (1450 W/ 115 V, Applied Test Systems Series 3210), and temperature was monitored using a K type thermocouple (Omega) placed outside the reactor immediately next to the position of catalyst bed. Temperature was controlled with a PID temperature controller (Love Controls, Series 16A). Liquid feed solution was introduced into the reactor with co-feeding of He in an up-flow configuration. A HPLC pump (LabAlliance, Series 1) was used to control the liquid feed rate. Gas flow was controlled with a mass-flow controller (Brooks 5850 model), and the system pressure was maintained at 300 psig by passing the effluent gas stream through a back-pressure regulator (GO Regulator, Model BP-60). The effluent liquid was collected in a gas-liquid separator and drained periodically for analysis by GC. Carbon balances closed within 5% for all data points. . Reaction conditions were 5 wt% butyl levulinate in 2-butanol as feed, WHSV = 0.18 h^{-1}, 150 °C, 300 psig He. The catalyst was regenerated *in-situ* by calcination in 60 cc (STP)/min flowing air at 723 K for 4 h.

Analytical methods

Quantitative analyses were performed by gas chromatography (Shimadzu GC2010 with an FID and RTx-5 column). Identification of products was performed using a gas chromatograph-mass spectrometer (Shimadzu Corp., GCMS-QP2010S) equipped with a SHRXI-5MS capillary column (30 m × 0.25 mm × 0.25 μm).

References

1. J. C. Serrano-Ruiz, J. Luettich, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso, *Journal of Catalysis*, 2006, **241**, 45-55.
2. M. A. Aramendía, V. Boráu, C. Jiménez, A. Marinas, J. M. Marinas, J. A. Navío, J. R. Ruiz and F. J. Urbano, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2004, **234**, 17-25.