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Catalytic acetoxylation of lactic acid to 2-acetoxypropionic acid, *en route* to acrylic acid

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1. Materials and Instrumentation

GC-MS analysis was performed using a Agilent 6890, Agilent 5973 Network Mass Elective Detector system, equipped with a 30 m × 0.25 mm i.d. Restex RTX® - 5 Amine fused silica capillary column, coated with Crossbond® 5 %/ diphenyl 95 % demethylpolysiloxane at 0.25 μm film thickness. The GC oven was programmed to start at a constant temperature of 50 °C for one minute, then to reach a temperature of 300 °C at a rate of 10 °C/min, it which temperature it was held for three minutes. Under these conditions, the retention times were around 6.0 minutes for di-silylated lactic acid (LA-TMS), 8.7 minutes for silylated acrylic acid (AA-TMS), 10.8 minutes for silylated 2-acetoxypropionic acid (2-APA-TMS) and 7.9 minutes for lactide. Products were analyzed by electron ionization (EI) mass spectroscopy (MS); LA-TMS: MS (EI): m/z 234 (M+, 1 %), 219 (27), 218 (24), 147 (43), 117 (100), 88 (9), 73 (70); for AA-TMS: MS (EI): m/z 144 (M+, 1 %), 129 (100), 75 (22), 73 (22), 55 (33); for 2-APA-TMS: MS (EI): m/z 189 (4 %), 147 (32), 129 (27), 117 (68), 73 (100), 43 (42); and for lactide: MS (EI): m/z 144 (M+, 1%), 57 (5), 56 (100), 45 (31), 43 (31).

^{1}H NMR spectra were recorded on a 400 MHz ^{1}H (100 MHz ^{13}C) Bruker AV400 spectrometer in deuterochloroform ($CDCl_3$) with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ) relative to $CDCl_3$ (^{1}H: 7.26 and ^{13}C: 77.36)[1] Coupling constants, J, are reported in Hz. Abbreviations are used to express multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. The following spectra were recorded: for LA: δ H (400 MHz, $CDCl_3$) 5.74 (1 H, br s), 4.39 (1 H, q, *J* 7.0), 1.47 (3 H, d, *J* 7.0); for AA: δ H (400 MHz, $CDCl_3$) 12.33 (1 H, br s), 6.52 (1 H, dd, *J* 17.2, 1.4), 6.13 (1 H, dd, *J* 17.2, 10.4), 5.96 (1 H, dd, *J* 10.4, 1.4); for lactide: δ_H (400 MHz, $CDCl_3$) 5.05 (1 H, q, *J* 6.7), 1.46 (3 H, d, *J* 6.7); and for 2-APA: δ H (400 MHz, $CDCl_3$) 11.40 (1 H, br s), 5.07 (1 H, q, *J* 7.2), 2.11 (3 H, s), 1.50 (3 H, d, *J* 7.2).

2. Procedures for Catalyst Synthesis

The sodium form of the Faujasite zeolite (Na-Y) was exchanged into its ammonium form (NH_4-Y) by adapting a published procedure.[2] The Na-Y zeolite was suspended in 1 M $NH_4NO_{3(aq)}$ (20 mL g^{-1} zeolite) under stirring at 80 °C. After 3 h, the solid was filtered, washed with water (4 × 20 mL) and dried for 6 h at 120 °C. To convert the zeolite to the protonic form (H-Y), it was heated in nitrogen atmosphere to 550 °C at 5 °C min^{-1} and calcined at this temperature for 2 h, before switching to air for another 2 h calcination at 550 °C.

Mesoporosity was introduced to zeolite Y according to a published procedure.[3] First, an acid wash pre-treatment step was required for using a zeolite with a low Si/Al ratio of 5.1. The sodium form of zeolite Y was suspended in water (10 mL g^{-1}) and treated with citric acid (1 mmol g^{-1}) for 1 h at room temperature. It was then treated with an NH_4OH soln (0.37 M, 64 mL) containing cetyltrimethyl ammonium bromide (CTAB, 0.70 g) and stirred for 20 min at rt. The mixture was then heated to 150 °C under autogenous pressure for 10 h. The solid was filtered, washed with water, and dried. The pH was maintained between 9–11 to avoid desilication. Next, the dried product was heated in nitrogen atmosphere to 550 °C at a ramping rate of 5 °C min^{-1}, and kept at this temperature for 2 h to remove any occluded template. Subsequently, the atmosphere was switched to air for another 2 h at 550 °C to remove any residual carbonaceous species.

Sulfated zirconia (SZ) was pre-treated as follows: The commercial SZ powder was heated in nitrogen atmosphere to 450 °C at a ramping rate of 5 °C min^{-1} and calcined at this temperature for 5 h to obtain SZ-450. In a similar procedure SZ-650 was obtained by heating in nitrogen atmosphere to 650 °C at 5 °C min^{-1} and calcined at this temperature for 3 h.[4]

The mixed phase Mo–V–Te–Nb–O catalyst was prepared by adapting a previously published procedure.[5] Ammonium heptamolybate, telluric acid, vanadyl sulfate and niobium oxalate were dissolved in deionised water, and mixed in a molar ratio of 1:0.3:0.17:0.12. The resulting slurry was stirred for 15 min, before being placed in an oil bath at 80 °C to evaporate the water overnight. The resulting material was collected and dried at 100 °C for 24 h. Subsequently, the dry material was ground to a powder and heated under nitrogen flow to 500 °C at 5 °C min^{-1} for 2 h.

Sulfonic acid functionalized silica gel was synthesized by modifying previously published procedures.[2, 6] Silica gel (2 g; 60 Å, 0.063–0.200 mm) was suspended in toluene (20 mL) and stirred for 1 h at 115 °C. Then, 3-mercaptopropyltrimethoxysilane (10.0 mmol, 2.0 g) was added, under stirring at the same temperature. After 24 h the solid was filtered, washed with water (5 × 20 mL) and dried in air. The dry cake was re-suspended in 33% $H_2O_{2(aq)}$ (35 mL) in a closed vessel and stirred for 1 h at 60 °C. The solid was filtered, washed with water, and then suspended in 10% $H_2SO_{4(aq)}$ (35 mL). After stirring for 1 h at rt, the catalyst was filtered, washed with water (4 × 20 mL) and dried at 110 °C for 16 h.

Sulfonated carbonaceous catalysts from glucose and activated carbon were synthesized according to published procedures.[7] P-toluenesulfonic acid functionalized glucose (Glu-TsOH) was obtained by thermal treatment of a mixture of glucose (2g) and p-toluenesulfonic acid monohydrate ((TsOH), 2g), sealed in a 30 mL Teflon coated autoclave, maintained at 180 °C under autogenous pressure for 24 h. The obtained product was filtered, washed with water and ethanol and then oven-dried at 110 °C for 16 h. Sulfonic acid functionalized activated carbon (AC-SO3H) was obtained by thermal treatment of suspended activated carbon (1g) in concentrated sulfuric acid (10 mL), sealed in a Teflon coated autoclave maintained at 180 °C under autogenous pressure for 24 h. The product was washed with hot distilled water (>80 °C) and filtered until the filtration water showed no sulfate ions, (i.e. pH ~ 7) and then dried at 110 °C for 16 h.

3. Analytical Method Development

Fig. S1 shows the linear response of LA-TMS against a large range of concentrations, with a R^2 value of 0.9975. The calibration plots of the other analytes showed similar accuracies and were used for all further quantitative experiments.

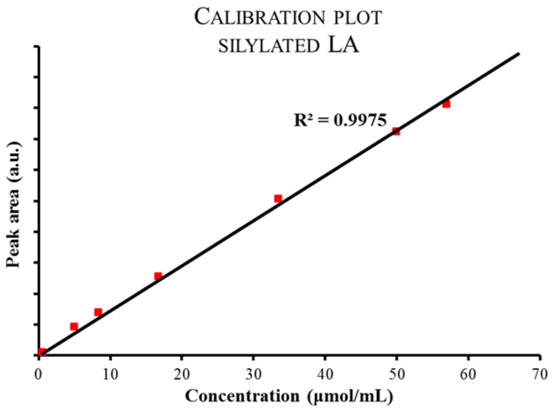

Fig. S1 Signal response of GC-FID against concentration of silylated LA. A typical initial concentration of LA-TMS in the analytical sample was around 50 µmol/mL.

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