Pausing a stir: heterogeneous catalysis in “dry water”

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Supporting Information

Experimental

Materials

The hydrophobic silica nanoparticles (H18) were kindly supplied by Wacker Chemie. Maleic and succinic acids (certified purities ≥99%), ruthenium catalyst (5 wt% loading on alumina, reduced) and deuterium oxide (for ^{1}H-NMR, 99.9 atom % D) were purchased from Sigma-Aldrich. Hydrogen gas (high purity, 99.995% minimum) was purchased from BOC Gases. The morphologies of the various dry water (DW) samples were observed using an Olympus CX41RF Microscope, fitted with a Linkam FDCS 196 variable temperature stage. Photographs were taken with an Olympus C-5060 digital camera.

Dry water reaction mixture preparation

Maleic acid (0.9577 g) was dissolved in deionised water (110 mL, 0.075 M), before pouring into a blender (Vitamix 2-Speed, 1.4 L polycarbonate jug). Hydrophobic silica (5.79 g, 5 wt% with respect to water) and ruthenium catalyst (0.1790 g, 1.625 gL^{-1}) were mixed by hand until homogeneous, and then added to the blender jug. Mixing was carried out at the higher speed setting (37,000 rpm) for 3x 30s bursts, with >1min periods between bursts to minimise droplet dissociation due to heat generated while mixing. The resulting pale grey powder could then be transferred between vessels by pouring.

Droplet size measurement

Average droplet size of dry water samples was determined by measurement of droplet images at 100x magnification, captured using microscope, camera and variable temperature stage. Calibration of measurements was achieved using 0.1 and 1 mm graticule slides, photographed under the same conditions as the dry water samples. In this instance, a total of 750 droplets were measured.

Hydrogenation (Figure S1)

Maleic acid dry water mixture (20 g) was loaded into a 50 mL capacity stainless steel pressure vessel (Parr Instrument Company, Moline, IL, USA), fitted with a pressure gauge, a High-Accuracy Gauge Pressure Transmitter (Cole-Parmer, 0–3000 psia) and a Type J Thermocouple (Parr, 0 –750 °C). The sealed vessel was placed in a distilled water circulator bath (HAAKE Phoenix C40P, Thermo Electron Corporation) set to 72 °C. Both thermocouple and transmitter were connected to a Digital Universal Input Panel Meter (Cole-Parmer), which communicates with a computer. A second pressure vessel fitted with a pressure gauge (600 mL capacity, Parr) was placed alongside in the bath, and purged with hydrogen gas three times before charging to 300 psia. This vessel would act as a constant-pressure hydrogen reservoir for the reaction vessel. The two vessels were allowed to equilibrate at 70 °C, before purging the reaction vessel three times with cylinder hydrogen. The vessels were then connected with stainless steel tubing, and the pressure adjusted to allow the reaction vessel to reach a constant reaction pressure of 300 psia. This point represented t = 0 on each reaction timescale. Individual reactions were allowed to proceed for 10, 20, 30, 60 or 120 min.

Control reactions were carried out as above, loading the reaction vessel with maleic acid solution (19 g, 0.075 M) and ruthenium catalyst (0.0309 g, 1.63 gL^{-1}) in place of dry water mixture.

Stirred reactions were carried out using a 68 mL capacity stainless steel pressure vessel (New Ways of Analytics, Lörrach, Germany) fitted with pressure and temperature sensors as above, in addition to a magnetic coupling (Minipower) connected to a T-shaped impeller. This vessel was loaded with maleic acid and catalyst as for control reactions above and sealed. For convenience, this vessel was heated using a thermostatically controlled oil bath to 70 °C. An overhead stirrer (IKA Eurostar Digital) was used to stir the reaction vessel at 1200 rpm. Stirring was halted while the reaction vessel was purged three times with hydrogen, and begun again once the reaction vessel had been connected to the reservoir and charged to 300 psia. This point represented t = 0 for stirred reactions.

Dry water dissociation can be achieved through mechanical compression of the sample, or by addition of water-miscible solvent in order to reduce the liquid surface tension to the point where hydrophobic interactions are no longer dominant. Both techniques are described below, however compression via centrifugation was favoured in order to avoid the use of additional chemicals.

1. Dry water reaction mixture was transferred to centrifuge tubes and centrifuged at 5000 rpm for 10 min (Eppendorf Centrifuge 5804). Dissociated reaction solution was then pipetted into ^{1}H-NMR tubes.
2. Dry water reaction mixture was added to methanol (50 mL, analytical grade) and stirred by hand until all dry water droplets had dissociated. The resulting mixture was then centrifuged for 1 min, before decanting off the reaction solution. Methanol was removed *in vacuo* prior to ^{1}H-NMR analysis.

Product analysis

Reaction solutions were analysed using ^{1}H-NMR (Bruker Avance, 400MHz), each with one drop of D_2O lock solvent. Comparative integration was carried out on singlet peaks observed for maleic acid (CH, δ = 6.21 ppm) and succinic acid (CH_2, δ = 2.52 ppm) to determine the extent of hydrogenation.

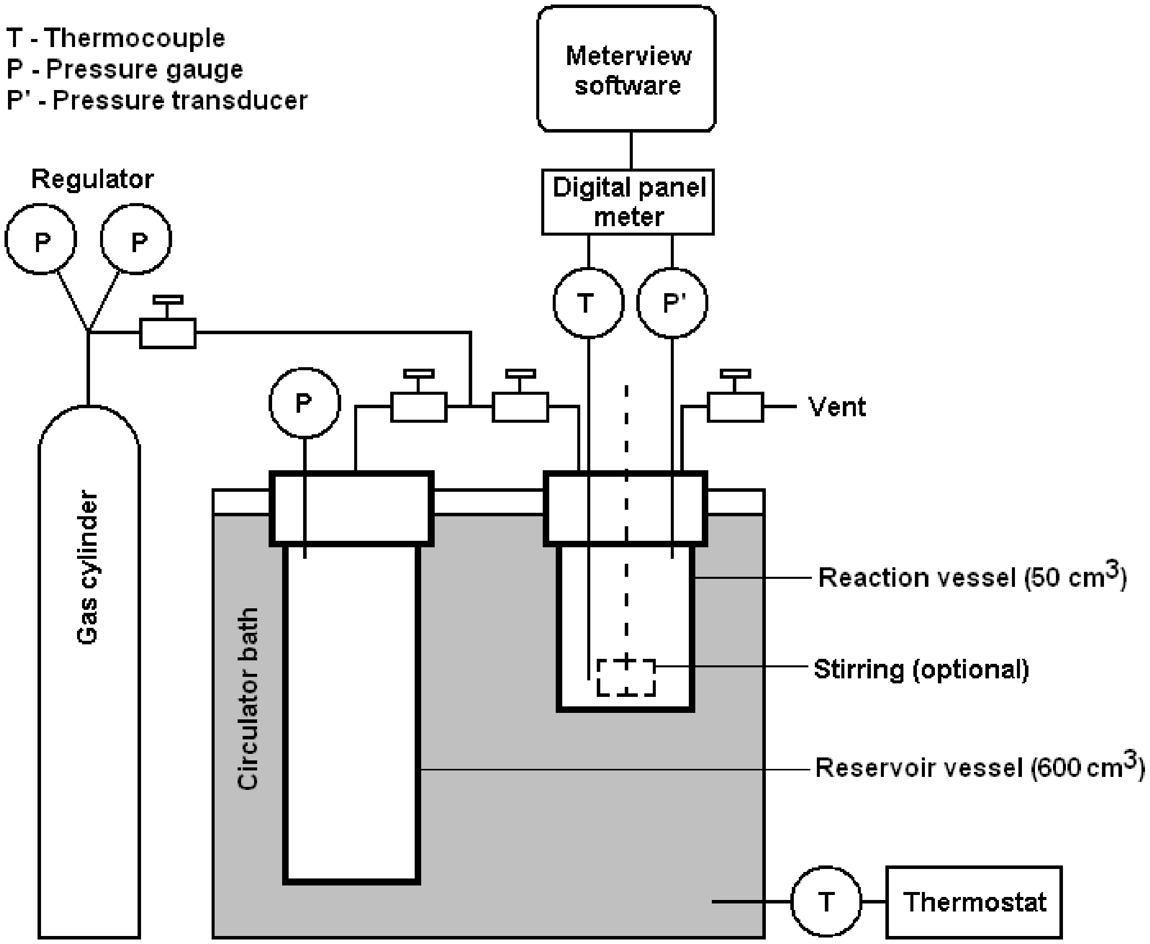

Figure S1. Schematic showing experimental hydrogenation apparatus.

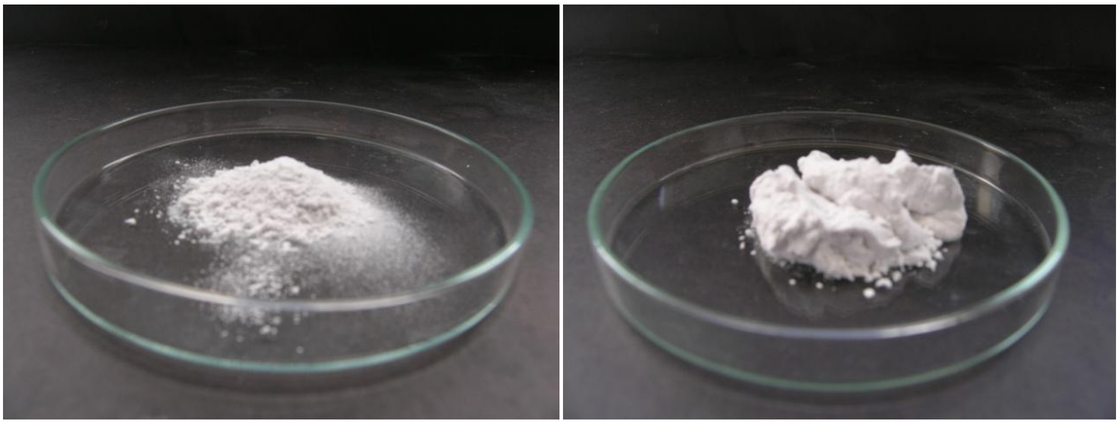

Figure S2. Samples of DW reaction mixtures prepared using recycled silica and catalyst. Recycled after 1 hr hydrogenation at 70 ^{o}C (left), and the same silica/catalyst recycled after a second hydrogenation (right). Samples showed increasing aggregation over multiple recycles.

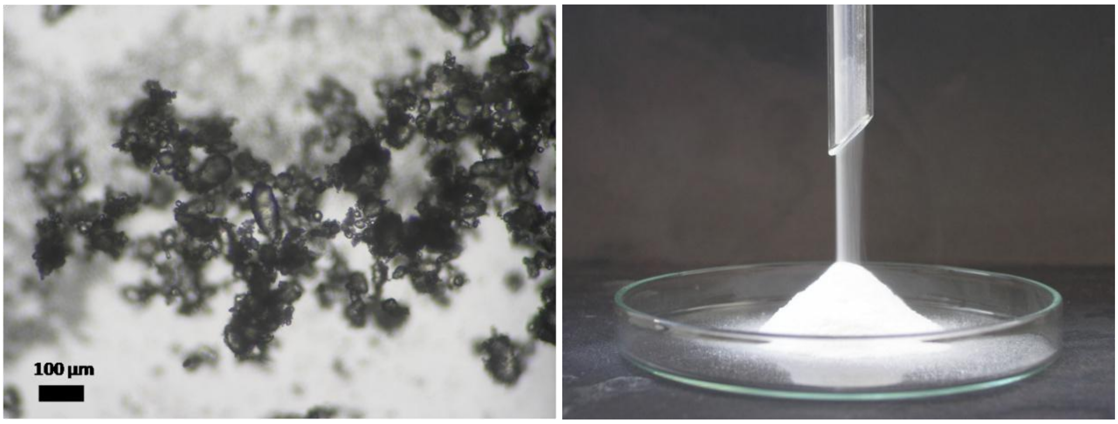

Figure S3. Photographs of DW prepared using succinic acid solution (0.075 M). Such DW is identical in all respects to those prepared with maleic acid and with pure water. Microscope image at 100x magnification.