

## Supporting Information for

# *Recycling of a Homogeneous Catalyst Using Switchable Water*

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## 1. General Procedures

Chemicals were used as received, except for styrene, which was passed through an inhibitor remover column (Sigma Aldrich) before use to remove the 4-*tert*-butylcatechol inhibitor. Conversions and selectivities were determined by gas chromatography (Shimadzu GC-17A with an Agilent DB-5 column) using calibration curves. High pressure reactions were performed in 31 mL Parr reaction vessels. <sup>31</sup>P NMR was performed using a 400 MHz Bruker instrument. Rhodium analysis was performed using a Varian 820 ICP-MS. pH measurements were taken with a Thermo Scientific Orion 4 Star pH meter.

## 2. Reaction & Recycling Procedure for the Hydroformylation of Styrene

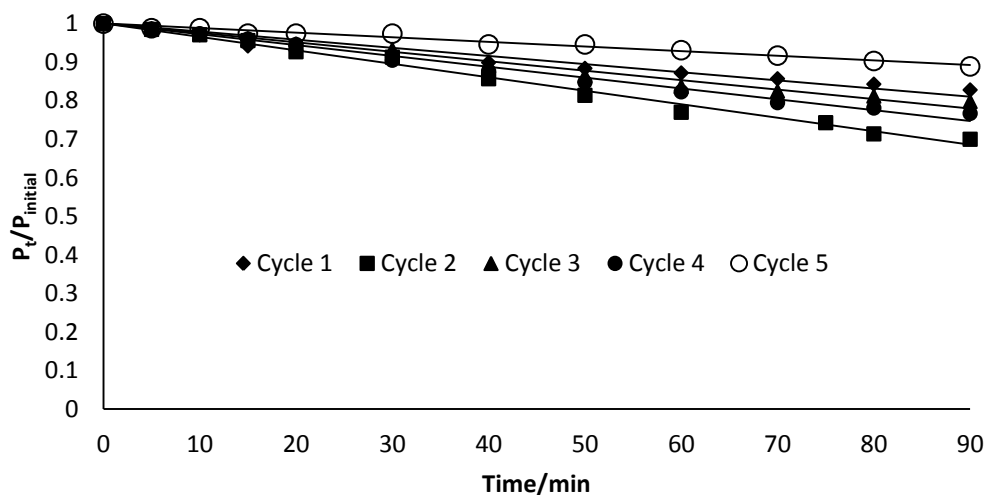
In a glass vial under N<sub>2</sub>, 6 mL degassed *tert*-butanol and degassed 4 mL deionized H<sub>2</sub>O were mixed. To this solution, 0.50 g of *N,N*-dimethylethanolamine or 0.47 g *N,N,N',N'*-tetramethyl-1,4-diaminobutane was added. Under N<sub>2</sub>, Triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt hydrate (TPPTS, 21 mg) and then chloro(1,5-cyclooctadiene)rhodium (I) dimer ([Rh(COD)Cl]<sub>2</sub>, 1.4 mg) were then dissolved into the mixture to give a clear, yellow solution. The uninhibited styrene (0.15 mL) was then pipetted into the aqueous mixture, which remained a single phase. The solution was transferred to a pressure vessel. The vessel was sealed and purged three times with synthesis gas (1:1 CO:H<sub>2</sub>). The vessel was heated to 100 °C and pressurized to 10 bar of synthesis gas. The reaction was run, with stirring, for 3 h.

After the reaction time, the vessel was cooled to 25 °C and the pressure was released. Under N<sub>2</sub>, the golden yellow clear solution was transferred to a glass vial and capped with a rubber septum. A long narrow-gauge steel needle was inserted through the septum into the solution. A second needle was inserted through the septum to act as a gas outlet. CO<sub>2</sub> was introduced into the solution via the first needle, while the solution was stirred, at a flow rate of ~ 10 mL min<sup>-1</sup> as measured by a J&W Scientific ADM 2000 Intelligent Flowmeter. CO<sub>2</sub> was bubbled through the solution for 30 min until a phase separation had occurred. The biphasic system consisted of a reddish brown, clear aqueous phase and a clear, colorless organic phase. Under a dynamic CO<sub>2</sub> atmosphere, the organic phase was extracted via

syringe and analyzed by gas chromatography. The aqueous phase was then stored under CO<sub>2</sub> atmosphere for later recycling. By-products of styrene hydroformylation were identified as ethylbenzene and acetophenone while 1-octene hydroformylation by-products were identified as octane and isomerized starting material. No 2-octanone was observed by GC for the hydroformylation of 1-octene.

To recycle the solvent and catalyst, the separated aqueous phase was placed in a 65 °C water bath and N<sub>2</sub> is introduced into the solution, with stirring, in a similar fashion to the CO<sub>2</sub> bubbling. After 45-60 min (45 for DMEA, 60 for TMDAB), the aqueous phase reverted back to a clear, yellow solution. The solution was cooled to 25 °C and under N<sub>2</sub>, 6 mL degassed *tert*-butanol and ~2 mL degassed H<sub>2</sub>O were added to return the system to its original volume. Fresh uninhibited styrene (0.15 mL) was pipetted into the mixture and the reaction procedure from above was repeated. The uptake of gas was monitored using an Omega Engineering Inc PG-2000 digital pressure gauge (Figure S1).

*Note:* The solvents were initially degassed via 3 freeze-pump-thaw cycles before reagent is added. All transfers and additions occurred under a dynamic N<sub>2</sub> atmosphere and solutions are stored under N<sub>2</sub> or CO<sub>2</sub>.



**Fig. S1** Ratio of pressure at time, *t*, over the total initial pressure (5 bar pressure of syngas (1:1 CO:H<sub>2</sub>)) for the hydroformylation of styrene (Table 1, Entry 4).

### 3. Salting Out of *tert*-Butanol by Switchable Water Additives

This procedure was adapted from the method described in an earlier paper on switchable water.<sup>1</sup> *tert*-butanol (1.5 g) and deionized water (1.5 g) were mixed together in a graduated cylinder. An amount of an amine additive was dissolved in the mixture to give a 0.80 molar (for TMDAB) or 1.40 molar (for DMEA) loading relative to water. A stir bar was added to the cylinder and the cylinder is capped with a rubber septum.

A single narrow-gauge needle was inserted through the septum and into the solution. A second needle was inserted into the septum but not into the solution so that it acted as a gas outlet. CO<sub>2</sub> was bubbled through the solution via the first needle at a flow rate of ~10 mL min<sup>-1</sup> while being stirred on a magnetic plate. Flow rates were measured using a J&W Scientific ADM 2000 Intelligent Flowmeter. CO<sub>2</sub> was bubbled through the solution for 30 min. After CO<sub>2</sub> treatment, the solution had undergone a phase separation. The volumes of both phases were recorded.

A known volume of each layer was extracted and placed in separate NMR tubes. The samples were dissolved in d<sub>3</sub>-acetonitrile and a known mass of 1,4-dioxane was added to each tube to act as an internal reference. The <sup>1</sup>H NMR spectra were then collected. From the known mass of the standard and

the integration of the *tert*-butanol or additive peaks, the amount of each in the NMR tubes was calculated. The concentrations in the NMR tubes were scaled up to that of the actual volumes to give the total amount of *tert*-butanol salted out from the aqueous phase and the amount of amine additive that was retained in the aqueous phase. Experiments were performed in triplicate.

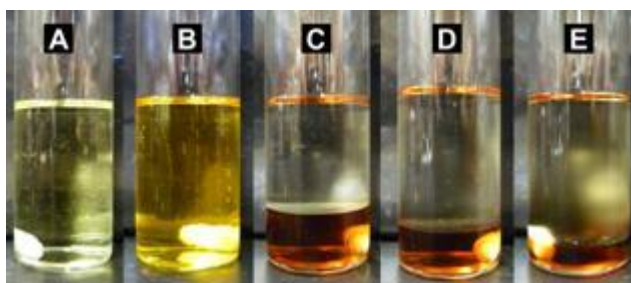
**Table S1.** Amount of *tert*-butanol salted out from 1:1 w/w solutions of *tert*-butanol and water with varied loadings of amines after 30 min of CO<sub>2</sub> treatment and the retention of the amine in the aqueous phase.

Additive	Loading	% <i>tert</i> -Butanol Removed	% Additive Retained
DMEA	1.4 molar	85 ± 1 %	79 ± 6 %
TMDAB	0.8 molar	81 ± 2 %	91 ± 2 %

The lower retention of the DMEA in the aqueous phase compared to TMDAB likely led to decreasing aqueous volumes upon CO<sub>2</sub> separation and increased leaching of rhodium metal observed in latter cycles (Figure S2 & Table S2).

**Table S2.** Concentration (mg/L) of leached rhodium in the organic phase after separation by switchable water as determined by ICP-MS. Samples were acquired from a typical reaction using DMEA as the switchable water additive.

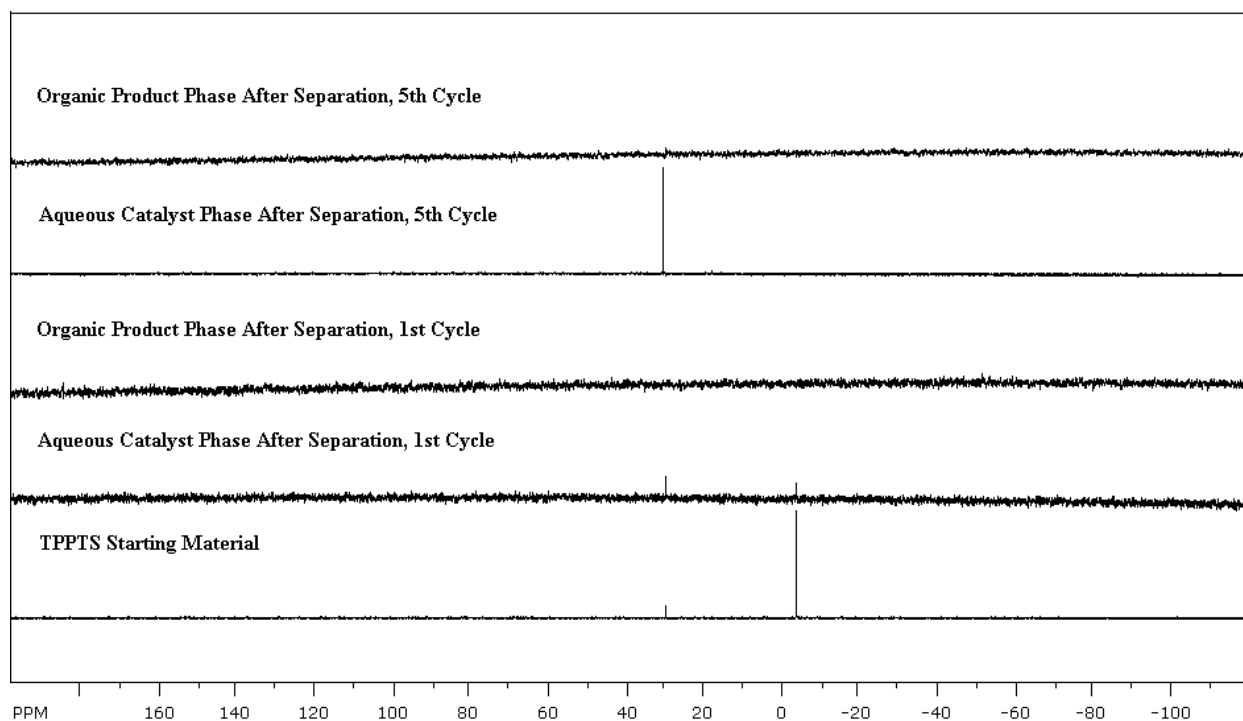
Cycle 1	Cycle 2	Cycle 3
1.07 ± 0.04	3.63 ± 0.04	10.12 ± 0.25



**Figure S2.** Cycling procedure for the hydroformylation of styrene using a typical 1.40 molar DMEA system. a) Solution before reaction. b) Solution after the reaction. c) Biphasic mixture after 30 min CO<sub>2</sub> treatment. d) Biphasic mixture after 30 min CO<sub>2</sub> treatment (2<sup>nd</sup> cycle). e) Biphasic mixture after 30 min CO<sub>2</sub> treatment (3<sup>rd</sup> cycle).

#### 4. <sup>31</sup>P NMR Spectra of Solvent System after CO<sub>2</sub>-induced Separation

No phosphines were observed by NMR spectroscopy to have leached into the organic products phases. However a peak of varying intensity representing oxidized TPPTS (~29 ppm) appeared in all of the aqueous extractions.



**Figure S3:**  $^{31}\text{P}$  NMR spectra of TPPTS starting material versus organic and aqueous layer after  $\text{CO}_2$ -induced separation from the first and fifth cycles of Table 1, Entry 3.

## 5. References

1. S.M. Mercer and P.G. Jessop, *ChemSusChem*, 2010, **3**, 467.