Electronic Supplementary Information

Tetronics/cyclodextrin-based hydrogels as catalyst-containing media for the hydroformylation of higher olefins

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Materials and methods

All chemicals were purchased from Acros, Strem or Aldrich Chemicals in their highest purity. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ^1H nuclei and 75 MHz for ^{13}C nuclei. $CDCl_3$ (99.50% isotopic purity) were purchased from Eurisotop. GC-MS analysis were performed using a Shimadzu GC-17A gas chromatograph using a Varian capillary column (length 30 m, internal diameter 0.025 µm) and a Shimadzu GCMS-QP500 mass spectrometer. All the hydroformylation experiments were carried out in laboratory reactors from Parr Instrument Company (USA). To prevent oxidation of the catalyst precursors, the reaction mixture was transferred into the reactor using the standard Schlenk technique.

Catalytic experiments

In a typical experiment, $Rh(CO)_2(acac)$ (3 mg, 0.012 mmol) was degassed three times by vacuum-N_2 cycles and dissolved in a degassed mixture of Tetronic®90R4, α-CD and water (6 mL). The resulting solution was stirred at room temperature until all the rhodium complex was dissolved (2 h). 1-dodecene (275 mg, 1.63 mmol) was poured into the autoclave and N_2-purged. The catalytic solution was then cannulated under nitrogen into the autoclave. Once the desired temperature was reached, the autoclave was pressurized under CO/H_2 (1/1) pressure (typically 50 bar) and the solution was vigorously stirred (2500 rpm). When the reaction was complete, the apparatus was allowed to cool down to room temperature and depressurized. The liquid products were cannulated under nitrogen into a flask while the catalyst-containing gel phase remained into the autoclave. The products were analyzed by ^1H and ^{13}C NMR experiments. All runs were performed at least twice in order to ensure reproducibility. The margin of error was <4%.

Recycling procedure

Once the products have been recovered, fresh substrate was added under nitrogen on the catalyst-containing gel. The autoclave was pressurized under CO/H_2 and the solution was vigorously stirred (2500 rpm). The procedure was repeated as needed.

Procedure for the synthesis of $HRh(CO)(TPPTS)_3$

In a Schlenk tube were dissolved 150 mg $Rh(CO)_2(acac)$ (0.58 mmol) and 1.2 g TPPTS (2,6 mmol, 5 equiv.) in 3 mL degassed water. The mixture was stirred under H_2 pressure (1 bar) for 4 h. A green-yellow solution was obtained. 25 mL ethanol were then added and a yellow precipitate was obtained. The precipitate was filtrated under nitrogen atmosphere and rinsed three times with hot ethanol to eliminate unreacted products. The resulting $HRh(CO)(TPPTS)_3$ complex was dried under vacuum for 2 h. Yield: 73% (752 mg).

Table S1 Physico-chemical properties of Tetronic®90R4 and Tetronic®701.

	Tetronics®90R4	**Tetronics®701**
Mw (g/mol)	7200	3600
Viscosity (cp at 25°C)	3870	600
Density (g/ml at 25°C)	1.05	1.02

Table S2 Optical photos of Tetronic®90R4/water solutions as a function of the Tetronic®90R4 concentration in 5 mL water without α-CD at 80 °C. S: solution; P: Precipitate; D: Demixing.

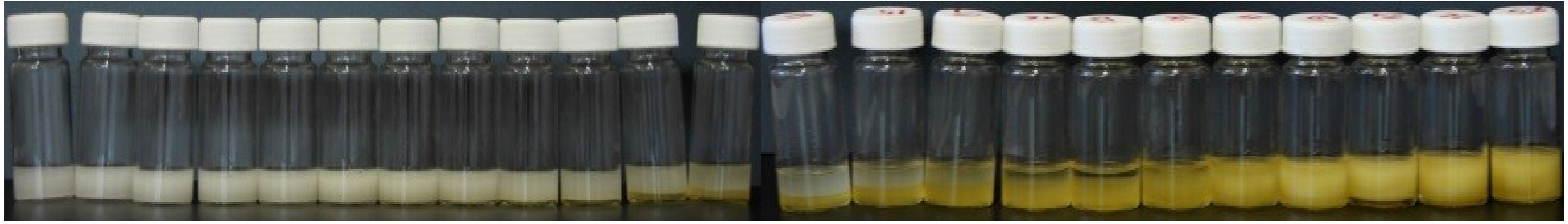
Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic®90R4 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	P	P	P	P	P	P	P	P	P	P	D	D	D	D	D	D	D	D	D	D	D	D	D

Table S3 Optical photos of Tetronic®90R4/α-CD/water solutions (870 mg α-CD, 6 mL water) as a function of the Tetronic®90R4 weight percentage at 25°C. P: Precipitate; G: Gel; D: Demixing.

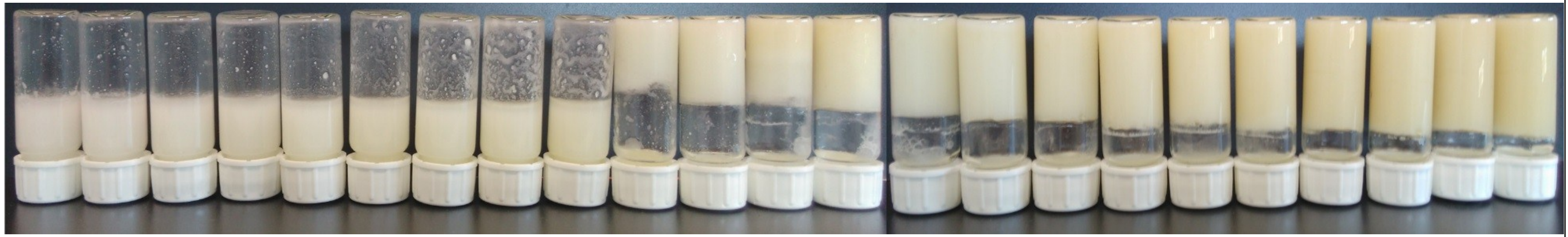
Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic ®90R4 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	P	P	P	P	P	P	P	P	P	G	G	G	G	G	G	G	G	G	G	G	G	G	G

Table S4 Optical photos of Tetronic®90R4/α-CD/water solutions (870 mg α-CD, 6 mL water) as a function of the Tetronic®90R4 weight percentage at 80°C. S: Sol; G: Gel;

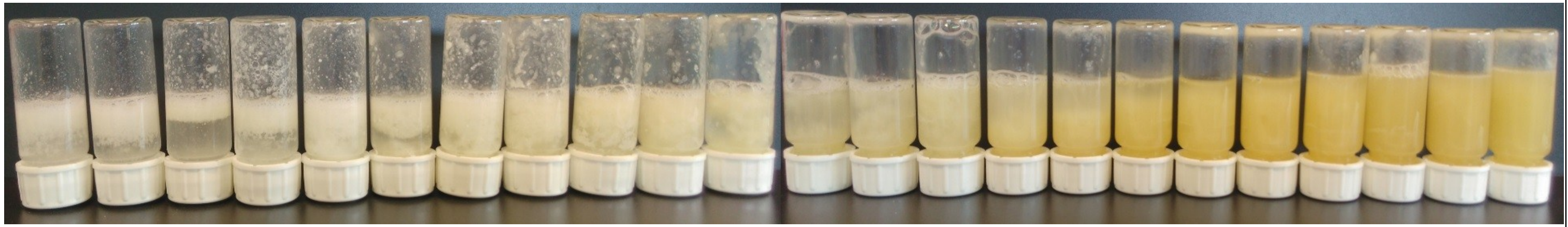
Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic ®90R4 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S

Table S5 Optical photos of Tetronic®90R4/α-CD/water solutions (870 mg α-CD, 6 mL water) as a function of the Tetronic®90R4 weight percentage after cooling down at 20°C the solutions depicted in Table S4. P: Precipitate; G: Gel; D: Demixing;

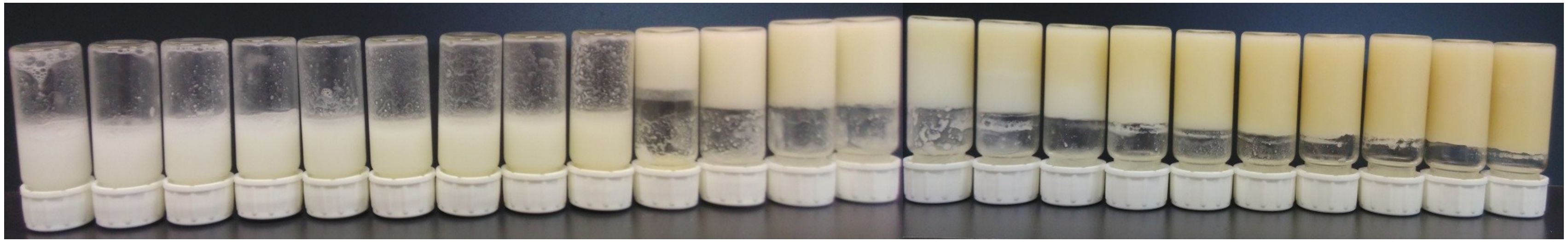
Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic ®90R4 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	P	P	P	P	P	P	P	P	P	G	G	G	G	G	G	G	G	G	G	G	G	G	G

Table S6 Optical photos of Tetronic®701/water solutions as a function of the Tetronic®701 concentration in 6 mL water without α-CD at 80 °C. S: solution; P: Precipitate; D: Demixing.

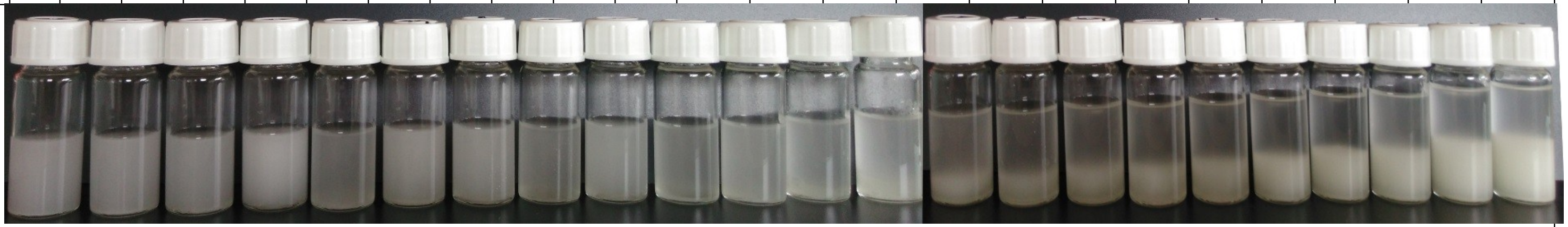
Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic®701 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	P	P	P	P	P	P	P	P	P	P	P	P	P	P	D	D	D	D	D	D	D	D	D

Table S7 Optical photos of Tetronic®701/α-CD/water solutions (870 mg α-CD, 6 mL water) as a function of the Tetronic®701 weight percentage at 25°C. P: Precipitate; G: Gel; D: Demixing.

Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic ®701 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	P	P	P	P	P	P	P	P	P	P	P	P	P	G	G	G	G	G	G	G	G	G	G

Table S8 Optical photos of Tetronic®701/α-CD/water solutions (870 mg α-CD, 6 mL water) as a function of the Tetronic®701 weight percentage at 80°C. S: Sol; G: Gel.

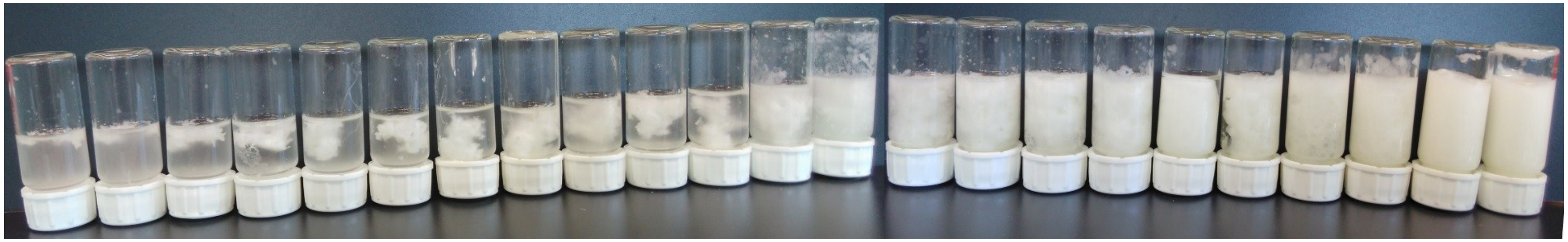
Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic ®701 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S

Table S9 Optical photos of Tetronic®701/α-CD/water solutions as a function of the Tetronic®701 weight percentage after cooling down the solutions obtained in Table S8 at 25°C. P: Precipitate; G: Gel; D: Demixing; 870 mg α-CD, 6 mL water.

Tube	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Tetronic ®701 (mg)	50	100	150	200	250	300	350	400	450	500	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500	3750
																							
Observation	P	P	P	P	P	P	P	P	P	P	P	P	P	G	G	G	G	G	G	G	G	G	G

Table S10 Variation of conversion, aldehyde selectivity and regioselectivity with the Tetronic®90R4 concentration in Rh-catalyzed hydroformylation of 1-dodecene.

Tetronic®90R4/H_2O (wt%)	**conversion (%)[b]**	**aldehyde selectivity (%)[b]**	**l/b[b,c]**	**Alkene isomers (%)**
1	25	73	2.3	27
4	29	83	2.5	17
10	36	92	2.5	8
25	67	92	2.4	8
30	75	93	2.5	7
35	81	99	2.4	<1
40	84	96	2.4	4
75	92	94	2.3	6

[a]Conditions: 1-dodecene (1.63 mmol), $Rh(CO)_2(acac)$ (3 mg, 0.012 mmol), TPPTS (33 mg, 0.058 mmol), α-CD (870 mg, 0.90 mmol), 6 mL H_2O, 80 °C, 50 bar CO/H_2, 1 h. [b]Conversions and selectivities were determined by ^1H NMR. [c]linear/branched aldehydes ratio.

Figure S1. ^{31}P NMR spectra of $HRh(CO)(TPPTS)_3$ in the sol phase under H_2 (1 bar) over time. a) t = 0; b) after 4 days.

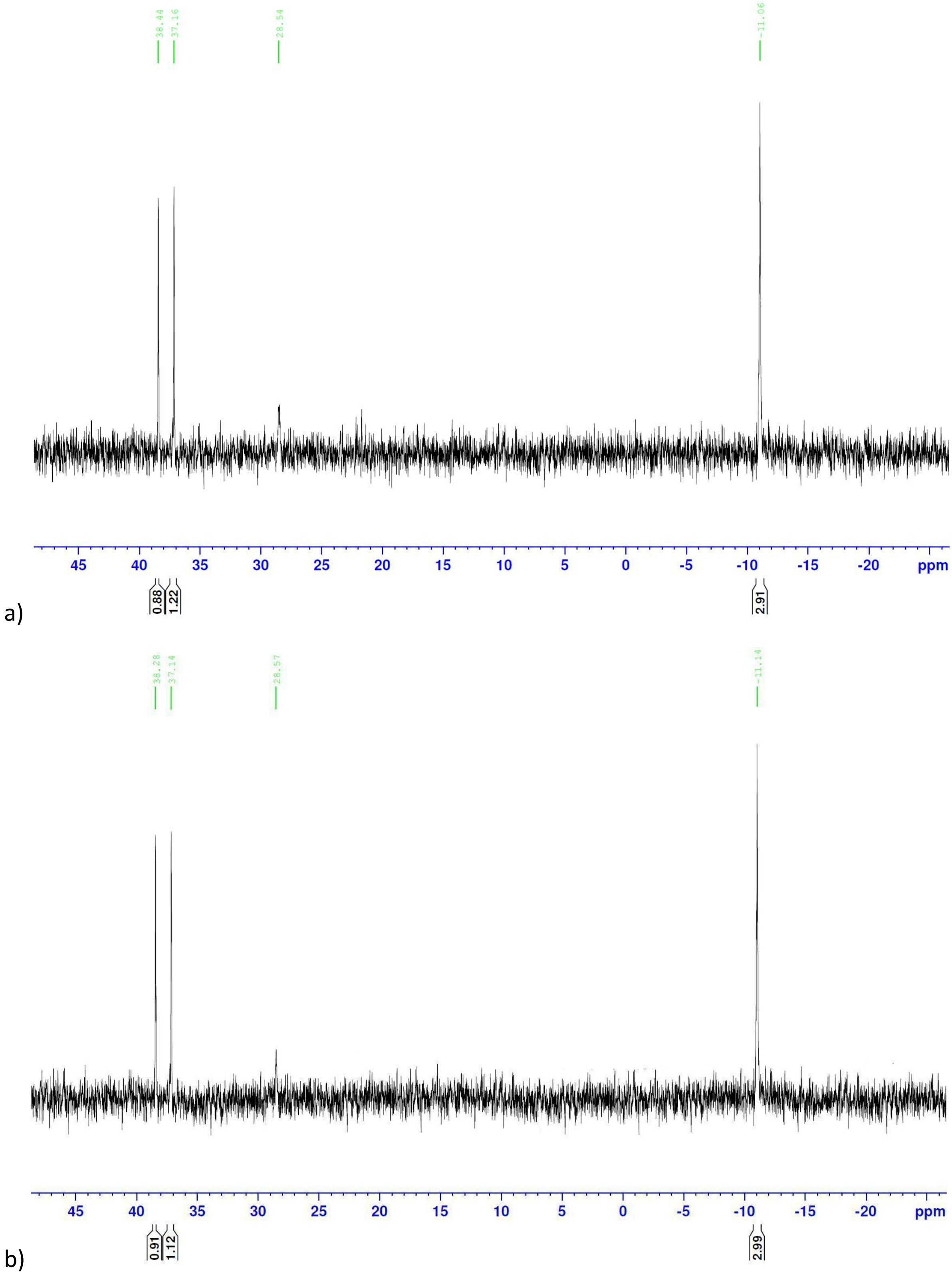


Figure S2. ^{1}H NMR spectrum of the organic phase after reaction.