Electronic Supplementary Information for

Investigation on heterogeneous Rh Catalysts for the Hydroformylation of 1,3-Butadiene to adipic aldehyde

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Table of Contents

1. A representative GC-MS chromatogram

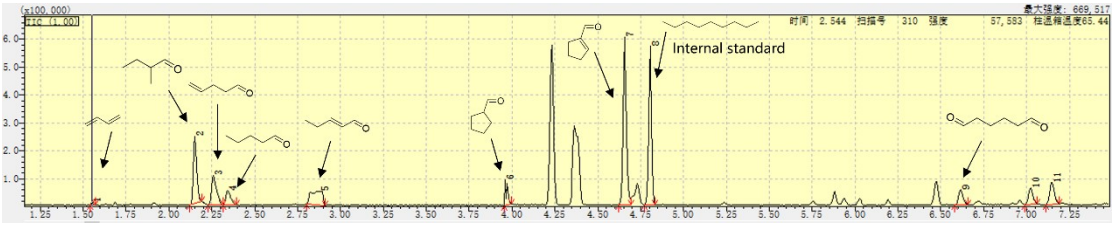


Fig. S1 Gas chromatogram of the reaction.

2. Supplementary electron micrographs

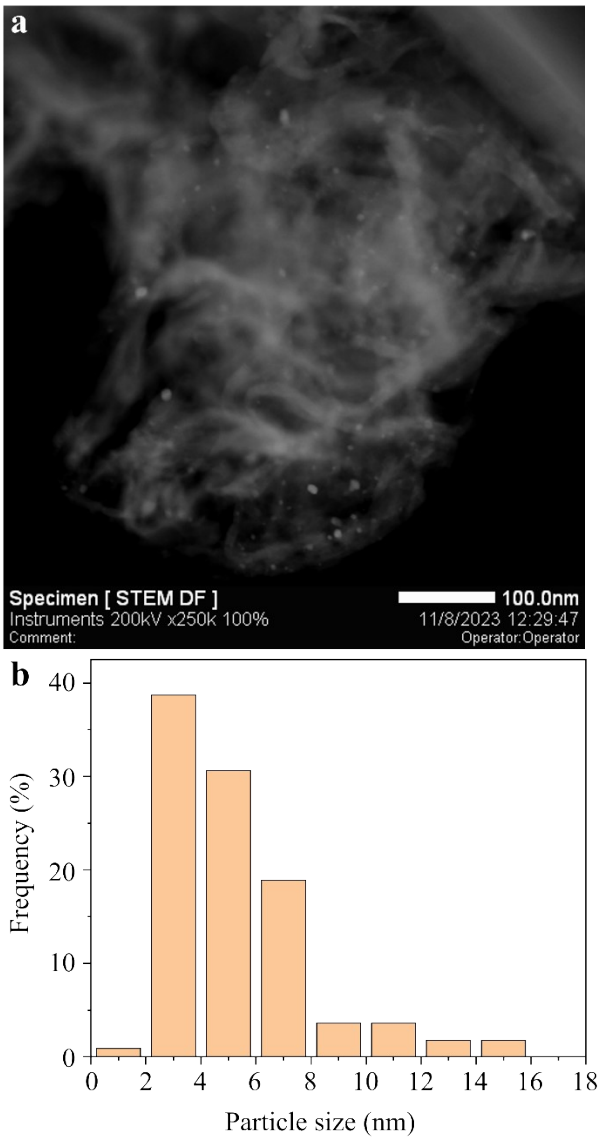


Fig. S2 (a) HAADF-STEM image and (b) particle size frequency distribution diagram of Rh/g-C_3N_4 (6.41 wt%).

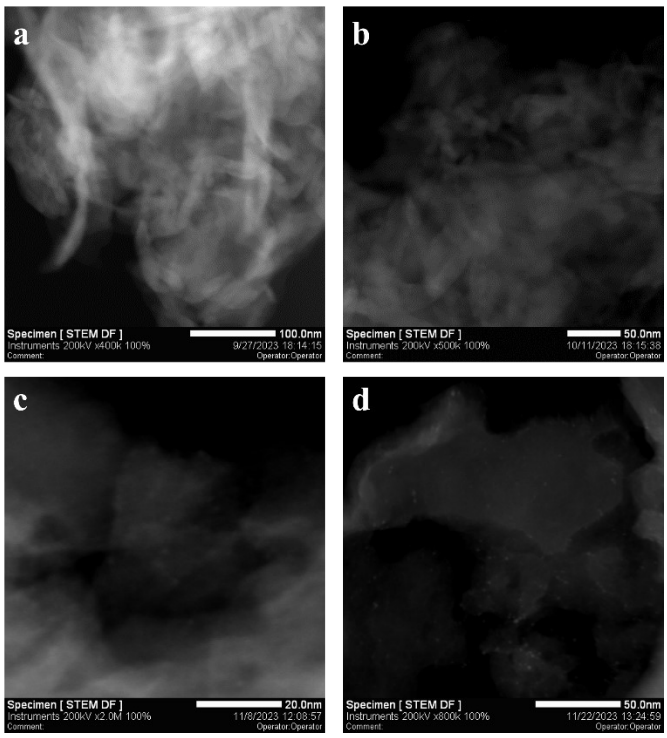


Fig. S3 HAADF-STEM images of (a) L11-Rh/g-C_3N_4 (1.0wt%) before reaction, (b) L11-Rh/g-C_3N_4 (1.0wt%) after the second recycle, (c) Rh/g-C_3N_4 (1.7wt%) and (d) Rh/g-C_3N_4 (3.49wt%).

3. Solid-state ^{31}P MAS NMR spectra

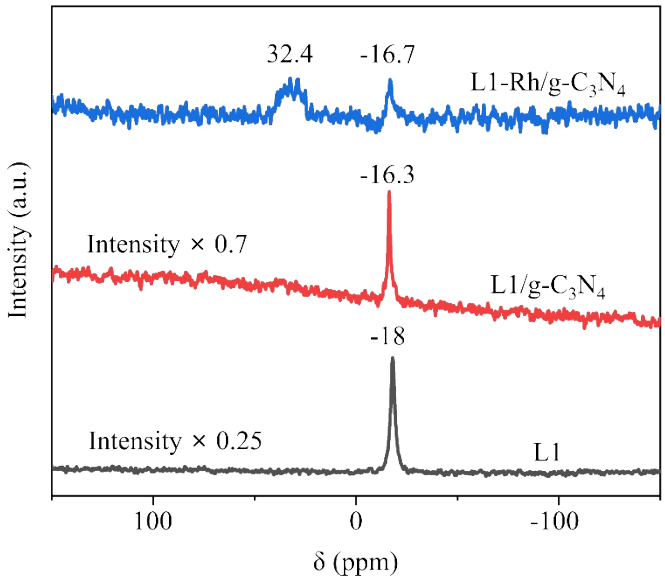
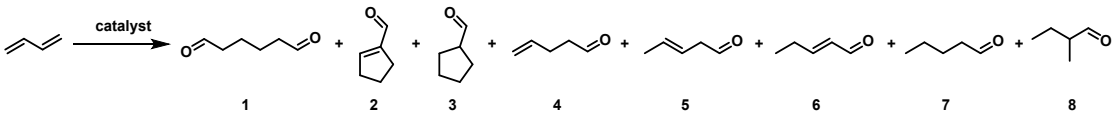


Fig. S4 Solid-state ^{31}P MAS NMR spectra of L1-Rh/g-C_3N_4, L1/g-C_3N_4 (obtained by impregnating g-C_3N_4 with L1 under standard Schlenk conditions) and L1.

4. Hydroformylation activity testing of 1,3-butadiene

Table S1 Effect of reaction temperature on the hydroformylation of 1,3-Butadiene by L11-Rh/g-C_3N_4.[a]

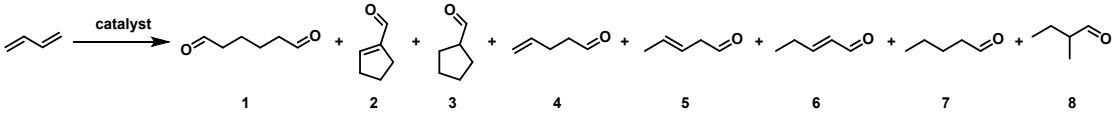


Entry	T/°C	Conv. (%)	Sel.[b](%)								Carbon balance %
			1	2	3	4	5	6	7	8	
1	110	100	1.5	0.4	15.4	6.2	5.7	0	53	17.8	95.1
2	100	99.7	8.5	0.6	10.8	0.5	10.3	0	66.1	3.2	92.3
3	90	98.1	13.7	0.1	3	0.5	8.4	0	56.8	17.5	98.7
4	80	95.9	11.8	0.7	0.3	3.9	56.1	0	27.2	0	93.9

[a] Reaction conditions: 1 g 1,3-Butadiene solution (6.21 wt% in toluene), 4 g toluene, 1 mol% L11-Rh/g-C_3N_4, 4 MPa CO/H_2 (1:1), 10 h.

[b] Selectivity of aldehyde products in the liquid phase.

Table S2 Effect of the initial CO/H_2 (1:1) pressure on the hydroformylation of 1,3-Butadiene by L11-Rh/g-C_3N_4.[a]

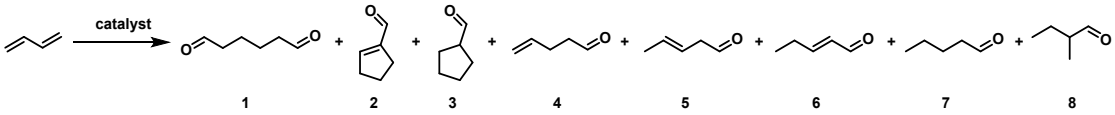


Entry	p/MPa	Conv. (%)	Sel.[b](%)								Carbon balance %
			1	2	3	4	5	6	7	8	
1	1	97.7	5.4	1.2	5.3	10.6	10.2	0	62.4	4.9	96.7
2	2	97.4	7	2.1	6.1	0	16.6	0	68.1	0.1	97.5
3	3	98.6	12.9	0.7	5.1	0	21.2	0	58.9	1.2	99.3
4	4	98.1	13.7	0.1	3	0.5	8.4	0	56.8	17.5	98.7
5	5	99.4	7.1	0	3.5	0	0	0	60.7	28.7	92.1

[a] Reaction conditions: 1 g 1,3-Butadiene solution (6.21 wt% in toluene), 4 g toluene, 1 mol% L11-Rh/g-C_3N_4, 90 ℃, 10 h.

[b] Selectivity of aldehyde products in the liquid phase.

Table S3 Hydroformylation of 1,3-Butadiene with different ligands. [a]



Entry	Catalyst	Conv. (%)	Sel.[b](%)								Carbon balance %
			1	2	3	4	5	6	7	8	
1	L1-Rh/g-C_3N_4 (1.0 wt%)	89.6	4.8	0.1	3.4	5.6	22.1	14.5	49.1	0.4	91.2
2	L2-Rh/g-C_3N_4 (1.0 wt%)	65.6	0	0	0	4.5	10.3	81.8	0	3.4	82.3
3	L3-Rh/g-C_3N_4 (1.0 wt%)	85.8	4	0.8	0	7.1	39	22.2	25.2	1.7	92.6
4	L4-Rh/g-C_3N_4 (1.0 wt%)	68.3	0	0	7.5	2.2	3	77.6	2.2	7.5	81.5
5	L5-Rh/g-C_3N_4 (1.0 wt%)	75.2	0.6	0.3	2.9	5.8	32.1	24.6	28.3	5.4	81.6
6	L6-Rh/g-C_3N_4 (1.0 wt%)	97.8	0	0	22.7	0.9	7	5.1	58.7	5.6	93.4
7	L7-Rh/g-C_3N_4 (1.0 wt%)	67.1	0	0	0	2.7	11.2	74.5	5.8	5.8	83.8
8	L8-Rh/g-C_3N_4 (1.0 wt%)	73.1	0	0	0	2.4	8.1	78.3	5.5	5.7	85.1
9	L9-Rh/g-C_3N_4 (1.0 wt%)	70	0	0	0	7.6	26.9	39.2	12.9	13.4	86.3
10	L10-Rh/g-C_3N_4 (1.0 wt%)	77.2	0	0	0	4.7	10.8	67.4	7.8	9.3	80.9
11	L11-Rh/g-C_3N_4 (1.0 wt%)	98.1	13.7	0.1	3	0.5	8.4	0	56.8	17.5	98.7
12 [c]	L11-Rh/g-C_3N_4 (1.0 wt%)	87.3	9.9	2	1.1	4.4	16.4	35.5	30.5	0.2	96.3

13 [d]	L11-Rh/g-C_3N_4 (1.0 wt%)	75.9	1.8	1.2	0	6.1	18.5	60.6	11.4	0.4	91.2
14	L11-Rh/g-C_3N_4 (0.23 wt%)	93.6	2	6.2	7	0.9	19.7	0	64.1	0.1	91.7
15	L11-Rh/g-C_3N_4 (1.7 wt%)	98.5	10.1	0.2	1.7	5.2	0	13.9	47.9	21	92.3
16	L11-Rh/g-C_3N_4 (3.49 wt%)	98.9	8.5	0.4	1.9	7.4	6.5	0	47.2	28.1	91.4
17	L12-Rh/g-C_3N_4 (1.0 wt%)	77.2	0	0.3	3.3	2.6	12.9	67.7	7.3	5.9	85.0
18	L13-Rh/g-C_3N_4 (1.0 wt%)	94.8	2.3	0.2	5	2.2	26.6	0	56	7.7	86.8
19	L14-Rh/g-C_3N_4 (1.0 wt%)	74.4	0	0	0	2.5	1.9	82.5	5.6	7.5	81.8
20	L15-Rh/g-C_3N_4 (1.0 wt%)	89	1.4	0.3	2.7	6.8	45	0	43.6	0.2	92.1
21	L16-Rh/g-C_3N_4 (1.0 wt%)	98.6	2	0	4.3	5	5.3	9.8	43.9	29.7	92.3
22	L17-Rh/g-C_3N_4 (1.0 wt%)	83.1	0.6	0.3	3.1	2.9	26.2	30.6	30.6	5.7	89.7
23	L18-Rh/g-C_3N_4 (1.0 wt%)	97.9	0	0	1.9	4	4.3	27.1	29.5	33.2	89.9
24	L19-Rh/g-C_3N_4 (1.0 wt%)	93.8	4.2	0.5	4.4	2.8	46.8	6.2	28.2	6.9	91.5
25	L20-Rh/g-C_3N_4 (1.0 wt%)	100	8.3	0.4	5.4	6.6	0	3.1	59.3	16.9	97.3

[a] Reaction conditions: 1 g 1,3-Butadiene solution (7.81 wt% in toluene), 4 g toluene, 1 mol% Rh catalyst, 4 MPa CO/H_2 (1:1), 90 ℃, 10 h.

[b] Selectivity of aldehyde products in the liquid phase.

[c] The first recycle of the catalyst L11-Rh/g-C_3N_4 (1.0wt%).

[d] The second recycle of the catalyst L11-Rh/g-C_3N_4 (1.0wt%).