Supporting Information for

One-step synthesis of N-coordinated Rh catalysts for efficient and stable alkene hydroformylation

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1. General Information

Chemicals and materials

Reagents were of analytical grade and used as purchased without further purification unless otherwise stated. $RhCl_3$ and melamine was obtained from Energy Chemical Co., Ltd, 1-octene (98%) and other olefins (**>** 97%) were bought from Shanghai Meryer Biochemical Technology Co., Ltd. The carbon nanotubes (CNTs) were purchased by Nanjing XFNANO Materials Technology Co., Ltd.

Instrumental measurements and physical characterization

The Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was performed to measure contents of Rh in all catalysts, using an Agilent 725-ES instrument.

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an ESCALAB 250xi X-ray photoelectron spectrometer with Al Kα X-ray radiation source (1486.6 eV) as the excitation source. All binding energies were calibrated by C1s peak at 284.6 eV.

Powder X-ray diffraction (PXRD) measurements patterns were characterized by Smartlab-SE (Japan) with a scanning angle (2θ) from 5 to 80° at a scan rate of 5°/min.

Nitrogen adsorption-desorption isotherms were measured at 77 K using an American Micromeritics ASAP 2460 automated gas sorption analyzer. The samples were outgassed at 200 °C for 6 h before the measurements.

Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method.

Thermogravimetric analysis (TGA) measurement was performed using a NETZSCH STA449F3 simultaneous thermal analysis system (Selb, Germany) under a nitrogen atmosphere at an increased rate of 10 °C/min from room temperature to 900 °C.

Raman spectra were performed at room temperature using a Horiba LabRAM HR Evolution equipped with 532 nm excitation lasers.

Transmission electron microscope (TEM) and High-resolution transmission electron microscope (HR-TEM) images were collected on a FEI TF20 transmission electron microscope operating at 200 KeV.

The aberration-corrected high angle annular darkfield STEM (AC HAADF-STEM) were obtained using the Thermo Fisher Titan Themis G2 300 with a 300 kV accelerating voltage.

In situ Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments for propene adsorption were conducted on a Bruker VERTEX 70 spectrometer with a narrow band MCT detector at a resolution of 4 cm^{-1} using 32 scans. The sample was treated at 200 °C in Ar atmosphere for 1 h to remove any adsorbed water. After the background spectrum of the sample was acquired at 80 °C, propene (7.5%

in Ar) was allowed to flow into the cell. The spectra of propene adsorption were recorded at different time. The CO adsorption was conducted at the same instrument, but exposing CO at -150 °C. The adsorption spectra were also recorded at different time.

2. Catalysts preparation

The pure CNTs were firstly pretreated with a 3:1 mixture of conc. H_2SO_4 and conc. HNO_3 at 50 °C for 3 h, and then washed with deionized water until the pH value reached 7. The oxidized CNTs (oCNTs) was dried at 50 °C to serve as a support. Secondly, 0.2 g of oCNTs well-dispersed in ethanol/water solution (v/v = 1:3, 40 mL) was slowly added dropwise to a mixture containing 1.0 g of melamine, 2 mL of formaldehyde solution and 5 mg $RhCl_3 \cdot 3H_2O$. After stirring at 100 °C for 3 h in an oil bath, the sample was collected by filtration, washing and desiccation. The dried mixture was finely ground and transferred into a tube furnace and heated to certain temperature with argon for 2 h at a heating ramp of 2 °C min^{-1}. The as-synthesized materials were denoted as Rh-N/CNTs-T (with T representing the calcination temperature, i.e. 700, 800, 900 or 1000 °C).

For comparison, Rh/oCNTs, Rh/g-C_3N_4, Rh/ZnO and Rh/TiO_2 were prepared by an incipient wetness impregnation method using $RhCl_3$ as the precursor. After drying at 80 °C overnight, the obtained powder was reduced by 10 vol % H_2/Ar at 250 °C for 2 h.

3. General procedure for the hydroformylation

The hydroformylation reaction of olefins was performed in an 80 mL stainless autoclave. Briefly, 20 mg of a catalyst sample was added into a 5 mL toluene solution containing 1.12 g of 1-octene. The reactor was sealed and flushed with syngas (CO/H_2 = 1:1) three times and then charged with 6 MPa syngas. The system was heated to the reaction temperature under continuous stirring. After the reaction vessel was cooled in an ice bath, the gas was released and hexadecane was added as an internal standard. The liquid product was qualitatively analyzed by gas chromatography (Agilent 7890 GC) equipped with an FID detector and a SE-54 column (30 m × 0.25 mm × 0.25 μm). The reactant conversion and product yield were calculated based on the following formulas.

$$X = \frac{N0 - N1}{N0} \times 100\%$$

$$Si = \frac{Mi}{Mo} \times 100\%$$

$$Yi = X \times Si \times 100\%$$

In the formulas, X represents the conversion of olefin. S_i and Y_i respectively denote the selectivity and yield of product i. N_0 refers to the total molar amount of the reactant olefin, N_1 is the molar amount of the residual olefin, M_i is the molar amount of product i, and M_0 is the molar amount of all the products.

For recycling, the Rh catalysts were separated by centrifugation, washed

with toluene, and used directly for the next run. The Rh contents of the used catalyst after each run were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The fixed-bed hydroformylation of 1-octene was performed to test the stability. The length of fixed-bed reactor was 40 cm and the inner diameter was 9 mm. The mixed solid catalyst of 0.2g Rh-N/CNTs-900 and 2.0g SiO_2 was thoroughly ground and then placed between two pieces of quartz wool. 5 wt% of 1-octene in toluene was pumped at a rate of 0.01 mL min^{-1} under a syngas atmosphere (CO:H_2 = 1:1, 120 °C, 6 MPa, 20 mL min^{-1}).

4. Catalyst characterization
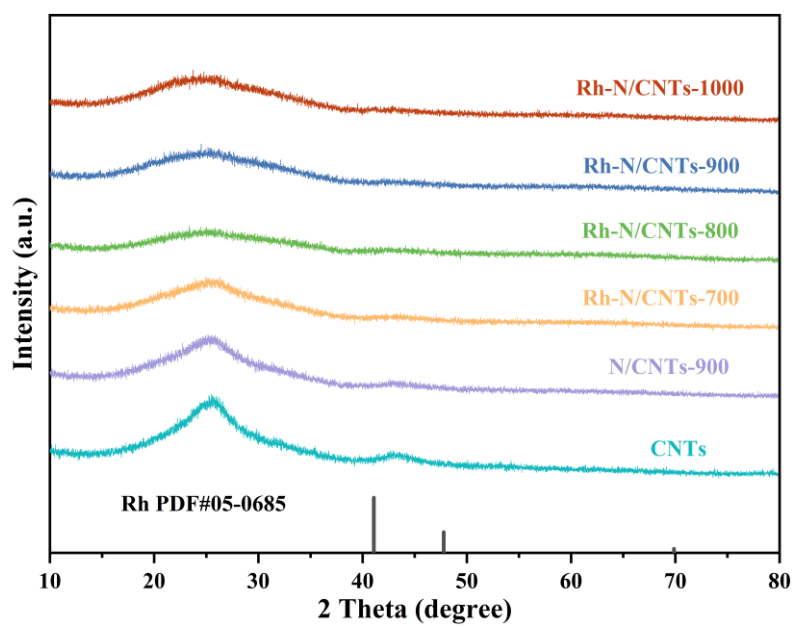
Figure S1. PXRD of all samples
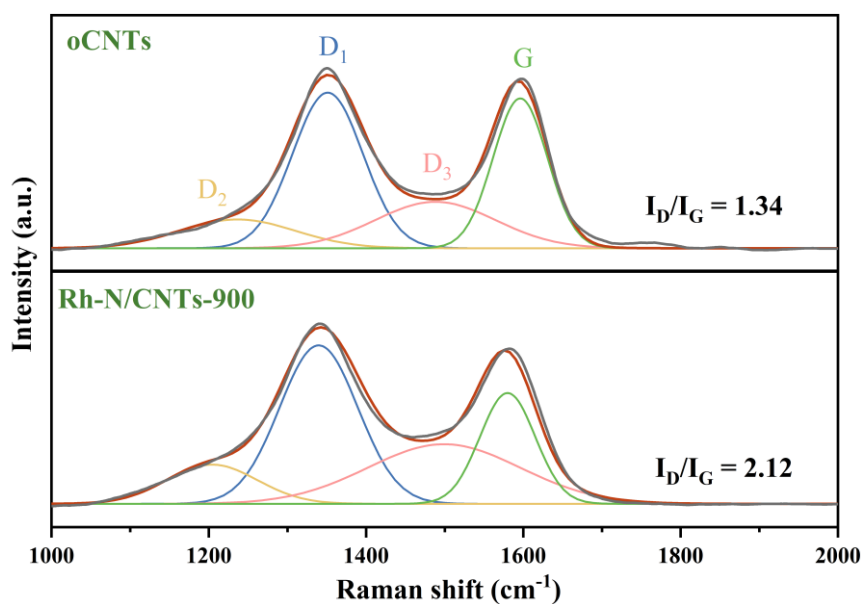
Typically, the degree of carbon material defect can be obtained from the integral strength ratio corresponding to D/G band. The results show that the I_D/I_G ratio of Rh-N/CNTs-900 (2.12) catalyst is significantly higher than that of the pure oCNTs (1.34). Therefore, the heat treatment process results in additional defects on the surface of Rh-N/CNTs-900, which is also consistent with the increase in the BET surface area.

Figure S2. Raman spectra of oCNTs and Rh-N/CNTs-900 samples.
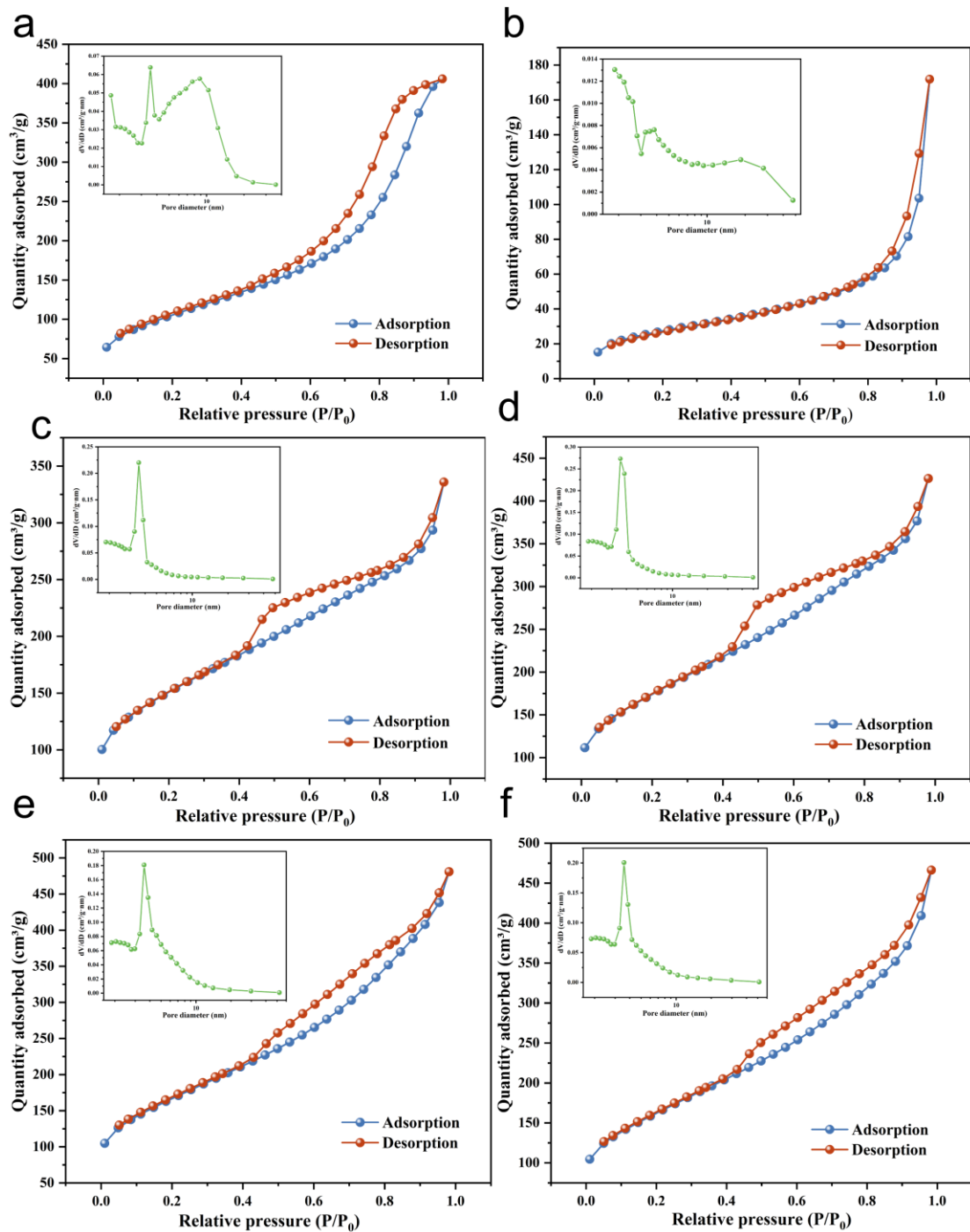
Figure S3. N_2 adsorption-desorption isotherm and pore size distribution of (a) oCNTs, (b) Rh-CN@CNTs, (c) Rh-N/CNTs-700, (d) Rh-N/CNTs-800, (e) Rh-N/CNTs-900, (f) Rh-N/CNTs-1000
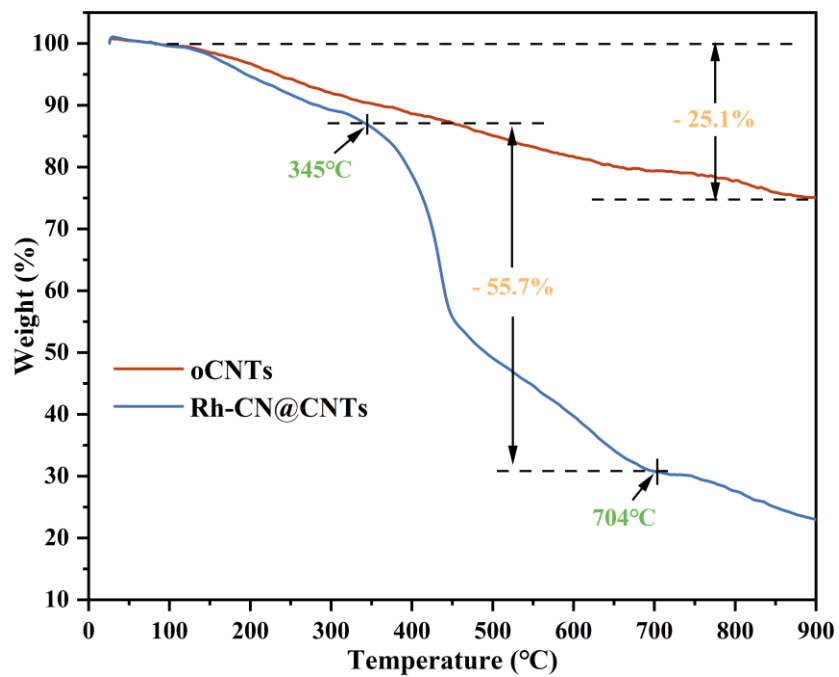
Figure S4. TG curve of CNTs and Rh-CN@CNTs
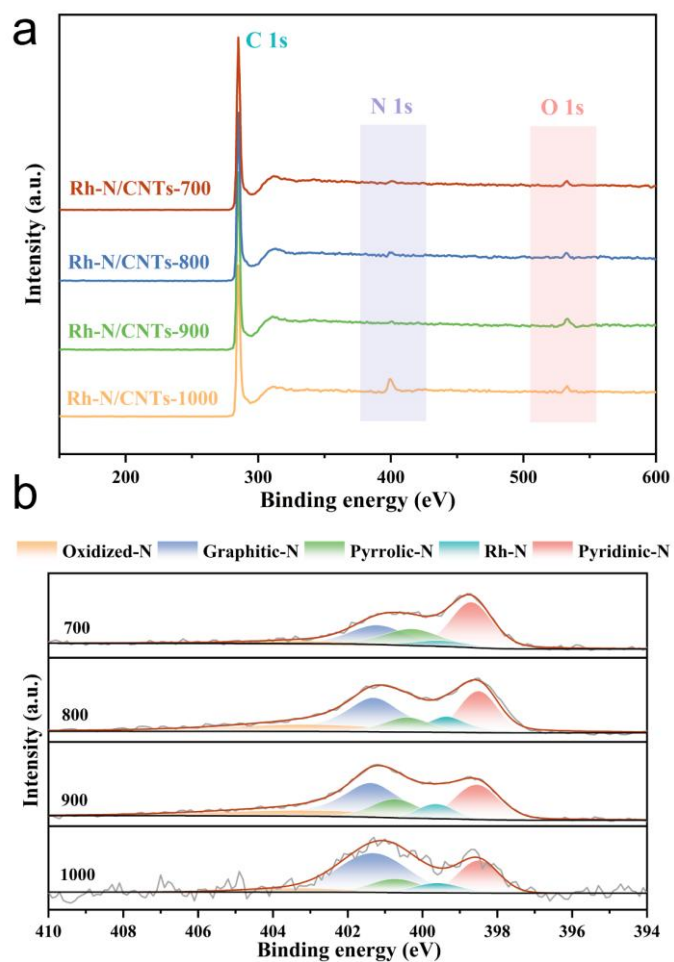
Figure S5. (a) XPS survey spectra and (b) N 1s XPS spectra of

Rh-N/CNTs-700, Rh-N/CNTs-800, Rh-N/CNTs-900 and

Rh-N/CNTs-1000.
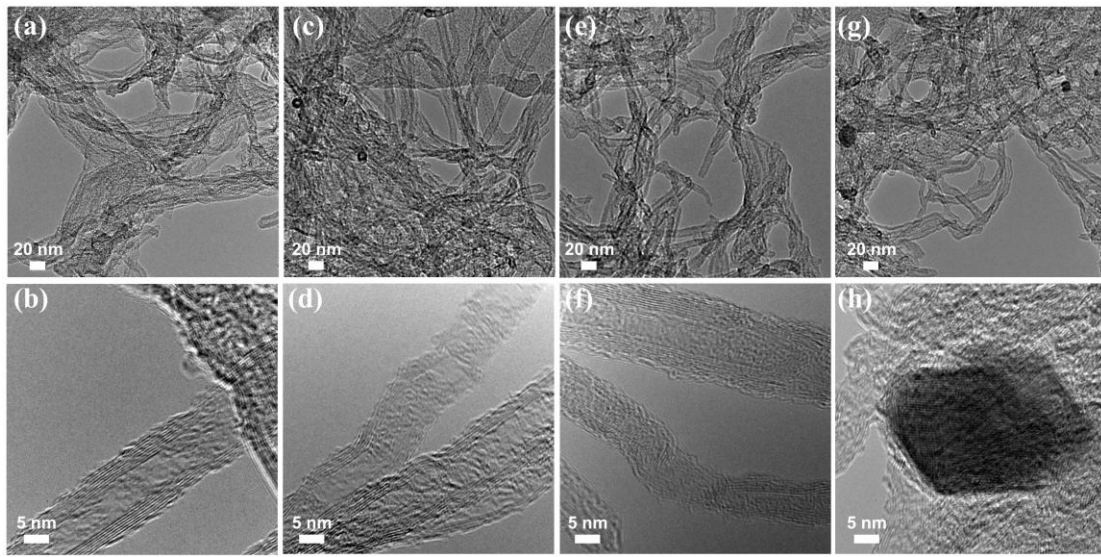
Figure S6. TEM and HRTEM images of (a, b) Rh-N/CNTs-700, (c, d) Rh-N/CNTs-800, (e, f) Rh-N/CNTs-900, (g, h) Rh-N/CNTs-1000.
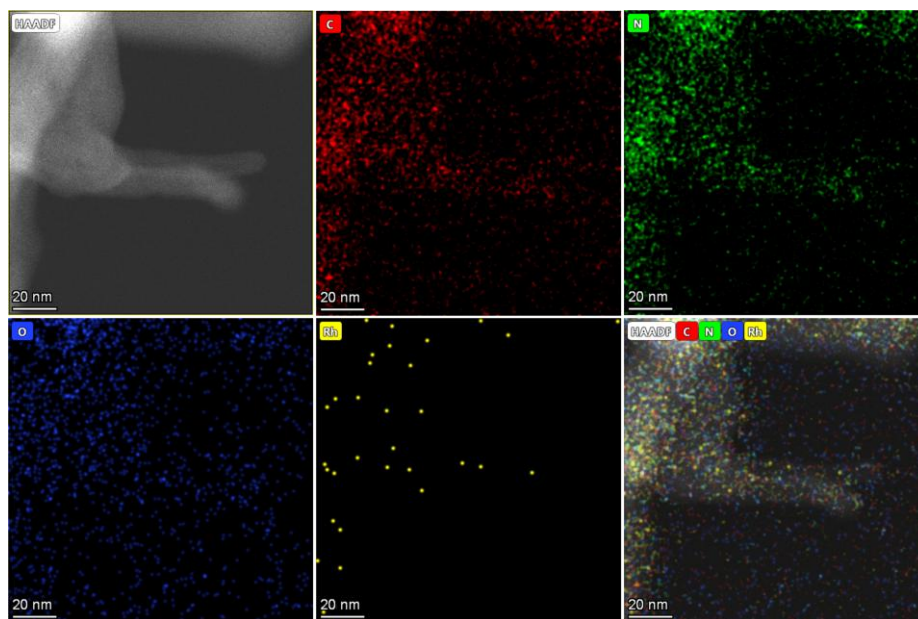
Figure S7. the elemental mapping images Rh-N/CNTs-900 catalyst.
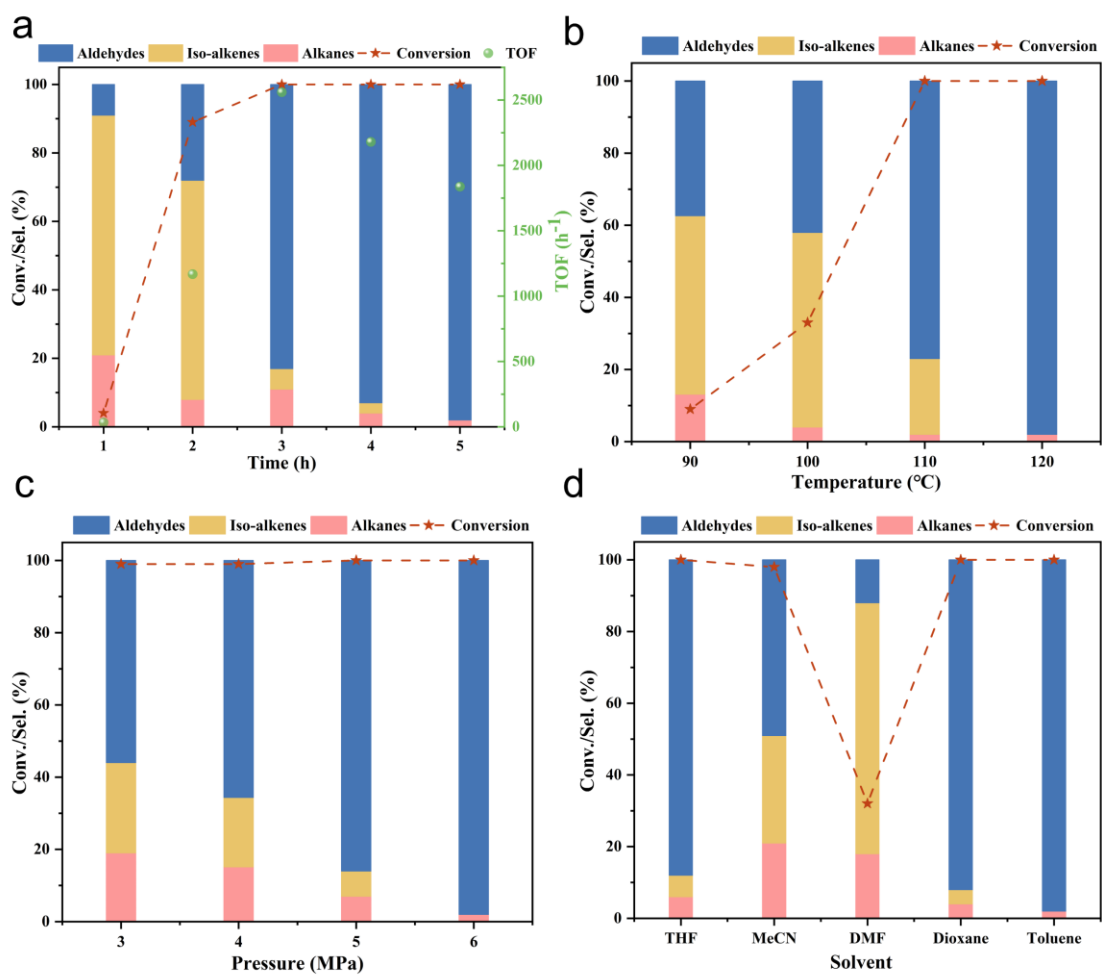
Figure S8. Screen of reaction condition of Rh-N/CNTs-900 catalyst, (a) reaction time, (b) reaction temperature, (c) reaction pressure and (d) solvent. Reaction conditions: 20 mg catalyst, 1-octene (10 mmol), toluene (5 mL), 120 ℃, 6 MPa, 5h.
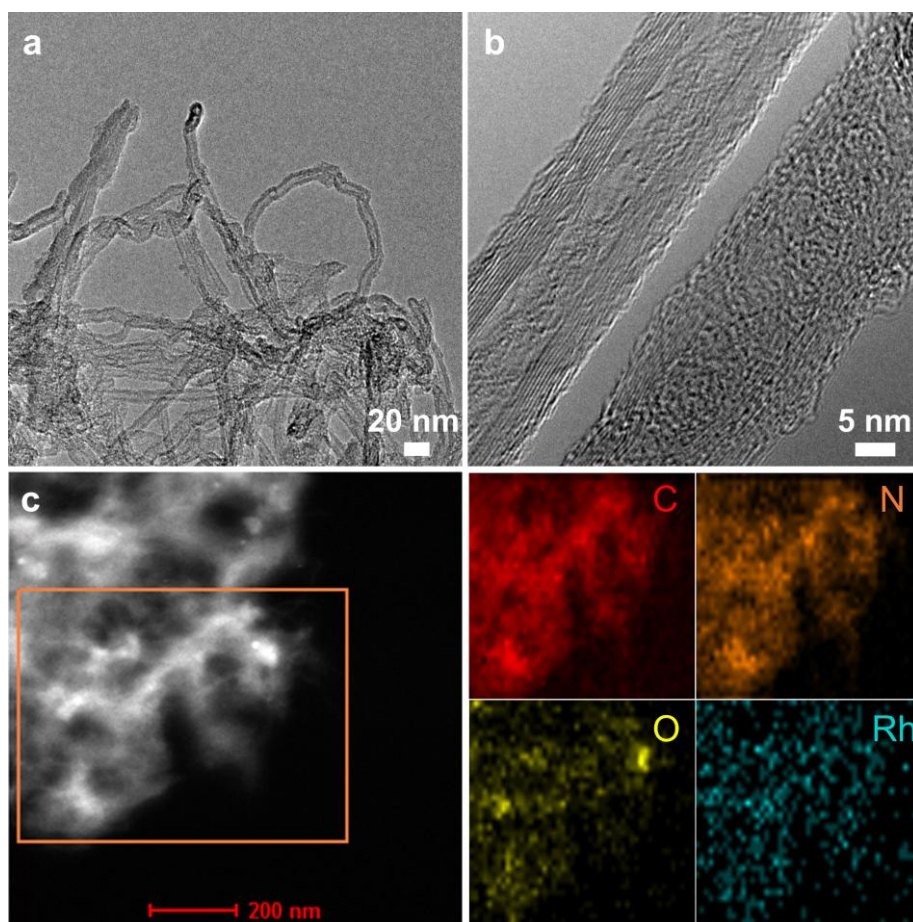
Figure S9. (a) TEM, (b) HR-TEM images and (c) STEM element mapping analyses of Rh-N/CNTs-900 after reaction.
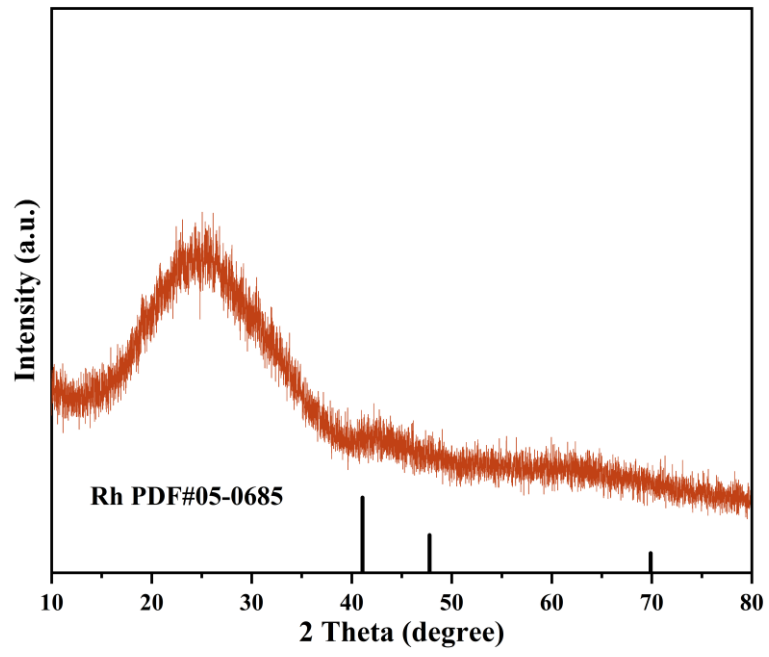
Figure S10. XRD patterns of Rh-N/CNTs-900 after reaction.
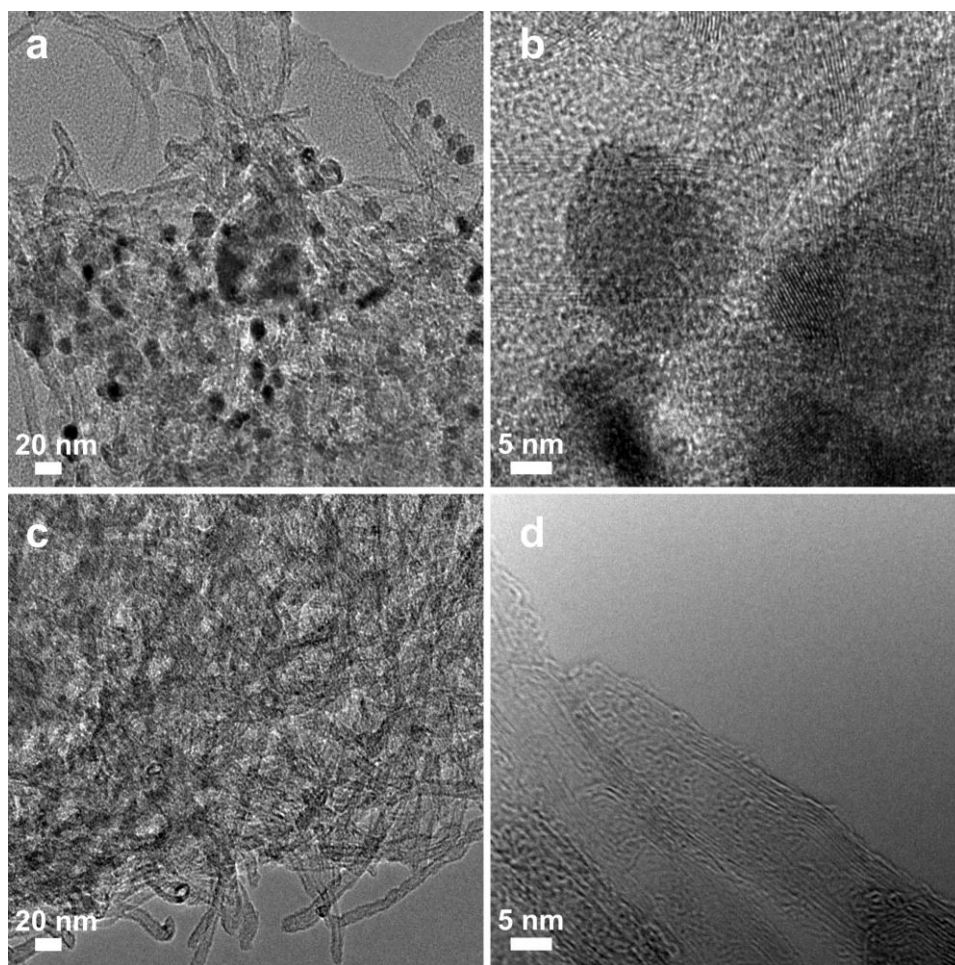
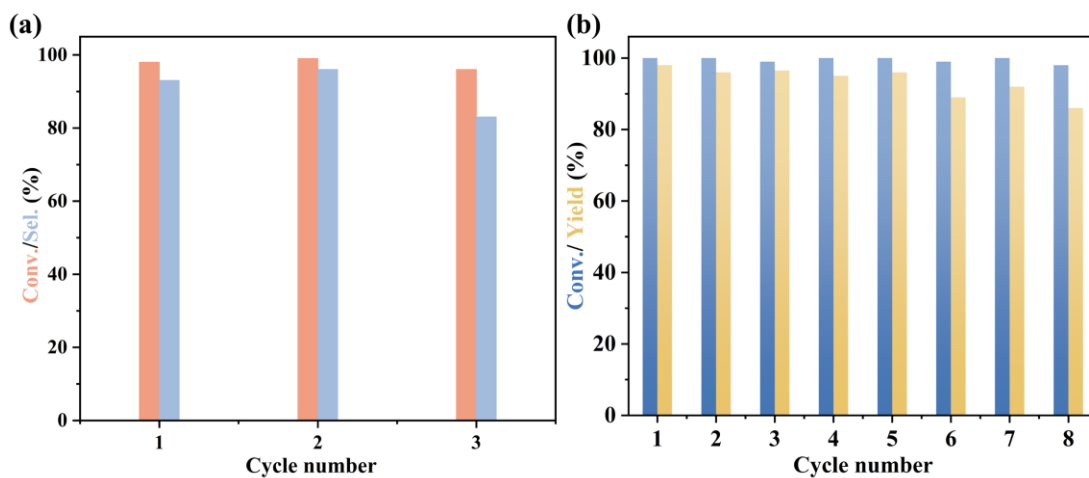**Figure S11.** TEM and HRTEM images of (a, b) fresh Rh/oCNTs, (c, d) used Rh/oCNTs.
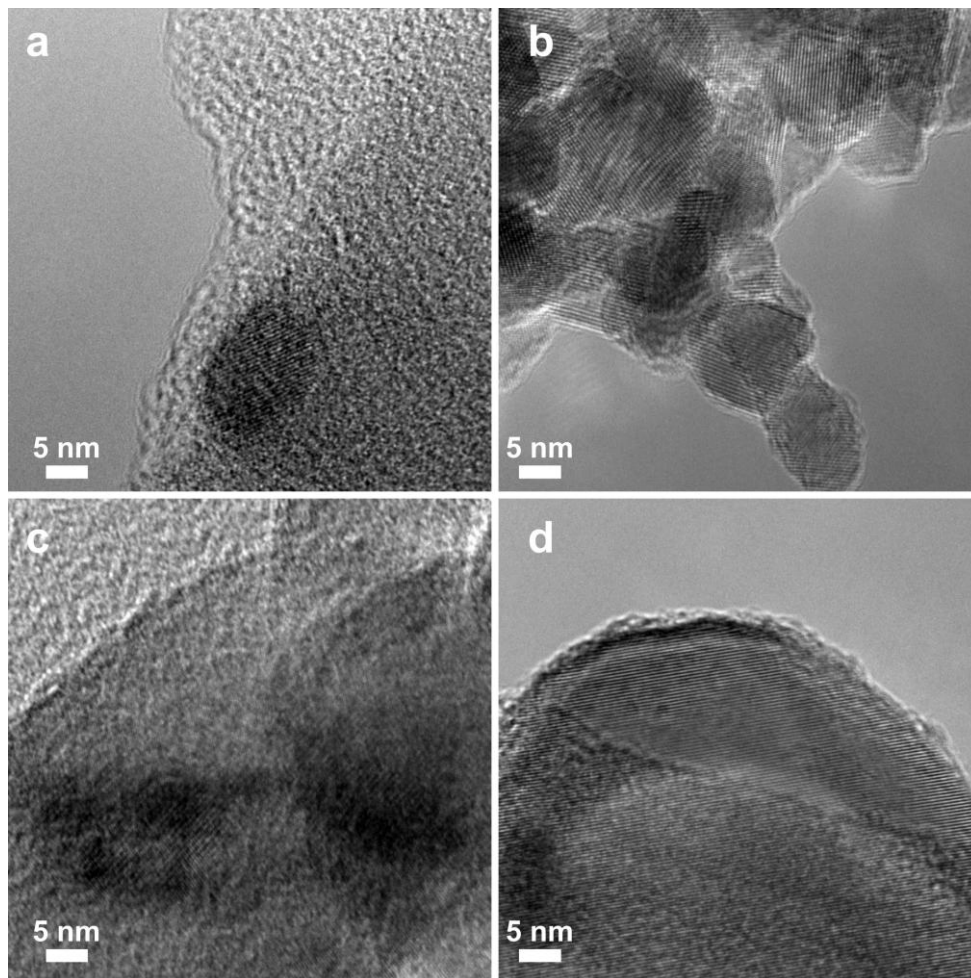
Figure S12. HRTEM images of (a) Rh/C_3N_4, (b) Rh/CeO_2, (c) Rh/TiO_2 and (d) Rh/ZnO.

As shown in Figure S13a-b, the catalytic activity of Rh-N/AC-900 catalyst is significantly worse than that of Rh-N/CNTs-900 catalyst. The primary reason might be attributed to microporous structure of activated carbon. The results confirm that it is justified to choose CNTs as support.

Figure S13. Cyclic stability of (a) Rh-N/AC-900 and (b) Rh-N/CNTs-900. Reaction condition: 20 mg catalyst, 1-octene (10 mmol), 120 °C, 6 MPa,5 h.
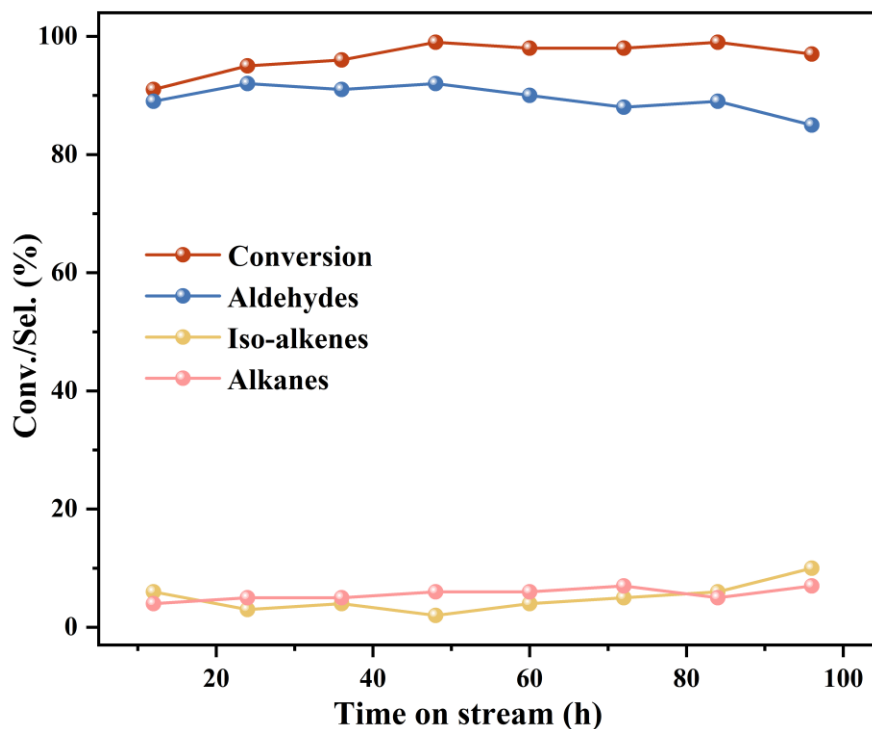
Figure S14. Hydroformylation of 1-octene in a fixed-bed reactor using Rh-N/CNTs-900 as the catalyst. Reaction conditions: catalyst 0.2g, substrate (0.01 mL min^{-1}), syngas (20 mL min^{-1}), 120 °C, 6 MPa.
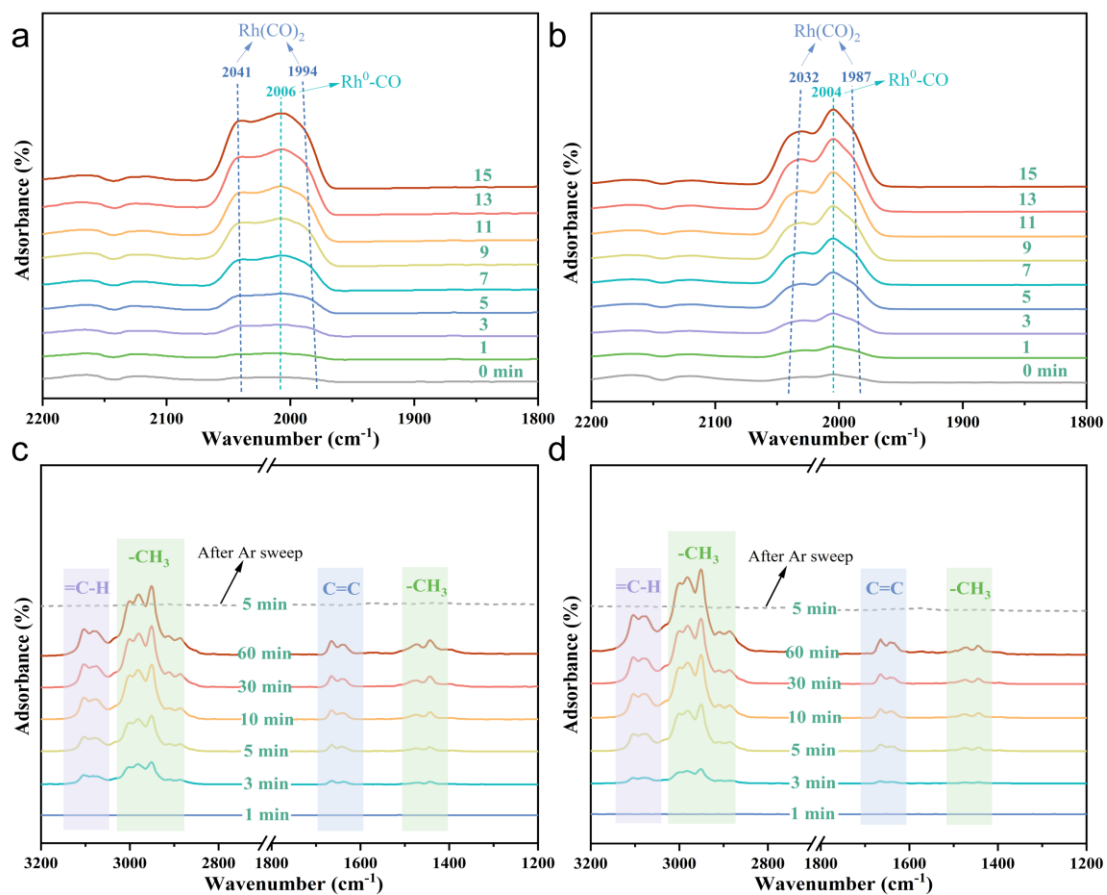
Figure S15. In-situ DRIFT spectra of CO adsorption over (a) Rh-N/CNTs-900 and (b) Rh/oCNTs, In situ DRIFT spectra of propene adsorption over (c) Rh-N/CNTs-900 and (d) Rh/oCNTs.

Table S1 The physical properties of as-prepared samples

Entry	Samples	S_{BET} ($m^2\,g^{-1}$)	Average pore size (nm)	Pore volume ($cm^3\,g^{-1}$)
1	oCNTs	382.0	6.8	0.60
2	Rh-CN@CNTs	99.2	12.5	0.26
3	Rh-N/CNTs-700	536.5	4.7	0.43
4	Rh-N/CNTs-800	621.3	4.7	0.58
5	Rh-N/CNTs-900	600.1	5.4	0.68
6	Rh-N/CNTs-1000	581.3	5.5	0.66

Table S2 Rh content determined by ICP-AES of various Rh catalysts with different used rounds.

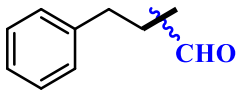| Entry	Catalyst	Rh (%)	Rh Residual metal (%)
1	Rh-N/CNT-900 fresh	0.56	
2	Rh-N/CNT-900 after one round	0.55	98.4
3	Rh-N/CNT-900 after four rounds	0.51	90.8
4	Rh-N/CNT-900 after eight rounds	0.45	81.0
5	Rh/oCNTs fresh	0.51	
6	Rh/oCNTs after one round	0.34	67.9
7	Rh/oCNTs after four rounds	0.22	42.4
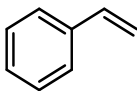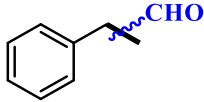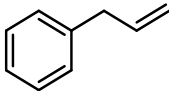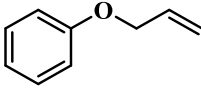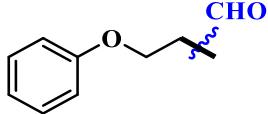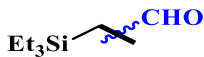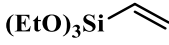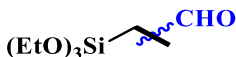
Table S3 N-species of Rh-N/CNTs-T samples obtained by XPS.

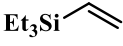| Samples	Total	N_1	N_2	N_3	N_4	N_5
Rh-N/CNTs-700	7.85%	7.6%	23.4%	22.5%	7.1%	39.4%
Rh-N/CNTs-800	5.35%	18.4%	36.1%	12.5%	7.7%	25.3%
Rh-N/CNTs-900	2.92%	15.2%	41.1%	14.0%	7.9%	21.8%
Rh-N/CNTs-1000	1.79%	10.4%	46.5%	12.1%	8.2%	22.8%

N_1: oxidized N, N_2: graphitic N, N_3: pyrrole N, N_4: rhodium-N, N_5: pyridine N

Table S4 Hydroformylation of various olefins using Rh-N/CNTs-900 catalyst. [a]

$$R \diagup\!\!\!= + CO/H_2 \xrightarrow{\text{Rh-N/CNTs-900}} R\diagup\!\!\diagdown CHO + R\diagup\!\!\diagdown^{CHO}$$

Linear aidehyde (L)   Branched aidehyde (B)

1   2
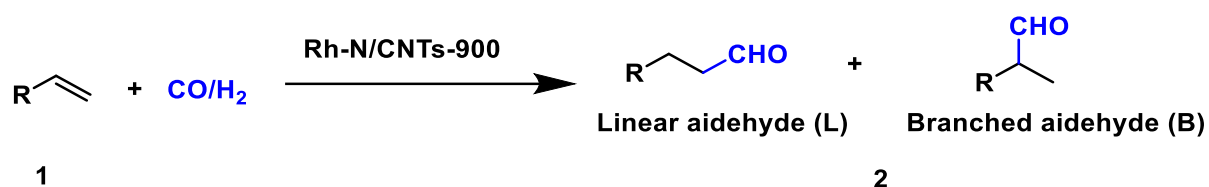
Entry	Substrate	Product	Conv. (%)	Yield (%)	L/B
1	1b	2b	100	98	0.8
2	1c	2c	100	98	0.7
3	1d	2d	100	98	0.8
4	1e	2e	96	93	0.7
5	1f	2f	92	92	-

6	1g	2g	100	98	1.1
7	1h	2h	95	93	1.2
8	1i	2i	-	78	-
9	1j	2j	-	78	-
10	1k	2k	-	72	-

[a] Reaction conditions: 20 mg Rh-N/CNTs-900 catalyst, toluene (5 mL), 120 °C, 6 MPa 5 h.1b ~ 1h were analyzed by GC, using hexadecane as the internal standard; 1i ~ 1k were analyzed by NMR, using triphenylmethane (1 mmol) as the internal standard.