Highly Uniform Rh Nanoparticles Supported on Boron Doped g-C_3N_4 as Highly Efficient and Recycle Catalyst for Heterogeneous Hydroformylation of Alkenes

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Contents

S.1 Experimental Section

Materials

All the reagents were of analytical grade and used without any further purification.

Preparation of pure g-C_3N_4

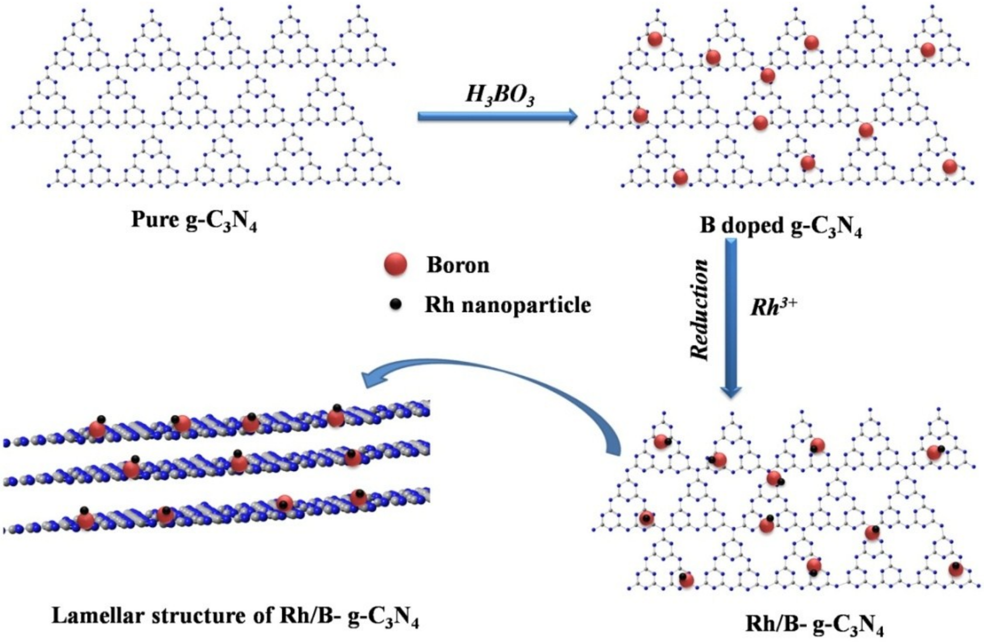
G-C_3N_4 was synthesized from urea by a facile template-free method as in our previous studies. [1]

Preparation of boron doped g-C_3N_4

The boron doped g-C_3N_4 with different B contents (1, 2, 3, 4, 5, 6 wt.%) were prepared and labeled as X%B-g-C_3N_4 (X = 1, 2, 3, 4, 5, 6). Typically, 0.5 g of the as-prepared g-C_3N_4 powder was dispersed in 20 mL of distilled water. After low-energy sonication for 0.5 h, the calculated amount of boric acid was added and continually stirred for another 6 h at 60 ^oC. The slurry was then dried in an oven at 80 ^oC. The obtained solid was calcined at 400 ^oC for 2 h in a muffle furnace to remove any impurities.

Preparation of boron doped g-C_3N_4 supported Rh-nanoparticle catalyst

The B-g-C_3N_4 supported Rh-nanoparticle catalyst (Rh/X%B-g-C_3N_4) was prepared via an impregnation-chemical reducing procedure using $RhCl_3 \cdot 3H_2O$ as the precursor. The preparation process of the Rh/X%B-g-C_3N_4 catalysts is shown in **Scheme S1**. Typically, 0.3 g of X%B-g-C_3N_4 were dispersed in 6 mL of $RhCl_3$ (2.47 mmol L^{-1}) aqueous solution, vigorously agitated for 24 h. After low-energy sonication for 2 h, the mixture was centrifuged. The obtained yellow solid were transferred into 100 mL flask with 10 mL of distilled water. Then 10 mL of freshly prepared $NaBH_4$ aqueous solution (17.76 mmol L^{-1}) was dropwise added, while vigorously stirred, into the mixture in ice-water bath. After addition of $NaBH_4$ aqueous solution, the mixture was continually stirred for another 1 h at 0 ^oC and room temperature, respectively. The mixture was centrifuged and the gray product was washed to neutral with distilled water repeatedly, and then washed three times with ethanol. The product was dried at 40 °C for 12 h in vacuum. For a comparison study, Rh/g-C_3N_4 was prepared using the similar method. The Rh loading of all the catalysts used in the present study was measured by ICP-AES; the contents of Rh were 0.25 wt.%.



Scheme S1 Illustration of the preparation process of the Rh/B-g-C_3N_4 catalysts.

Sample characterization

The morphologies and microstructures of the as-prepared catalysts were analyzed by transmission electron microscopy (TEM, Philips T20ST) and scanning electron microscopy (Shimadzu SS-550). The chemical states of Rh in catalysts were determined by X-ray photoelectron spectrometer (XPS, Thermo SCIENTIFIC ESCALAB 250Xi), and all binding energies were calibrated using C 1s (E_b = 284.6 eV) as the reference. The phase structures of catalysts were characterized with X-Ray Diffraction (XRD, D8 advance with Cu Ka radiation). The bulk Rh contents of samples were measured by ICP-AES (ICP, Thermo ICAP-Qc). Textural characterization of samples by N_2 adsorption was taken with a ASIQM0000-4 automatic gas adsorption instrument made in American Quantachrome company production.

Catalytic activity test

The catalytic hydroformylation reaction was carried out in a 60 mL stainless steel autoclave reactor equipped with a magnetic stirrer. In the typical experiment, the required amount of catalyst, substrate and solvent were placed into the reactor. The reactor was sealed and purged three times with syngas, and subsequently pressurized to the desired pressure. The reactor was heated to the reaction temperature and kept for the desired time under stirring. After the desired reaction time, the stirring was stopped, and the reactor was cooled to room temperature and depressurized. The reaction mixtures were withdrawn for GC analysis (GC-7900 A equipped with a flame ionization detector and a 30 m × 0.32 mm × 0.33 μm SE-54 column). Temperature of the injection point and FID detector was 200 ^{o}C and 240 ^{o}C, respectively.

S.2 XRD patterns of the as-prepared samples

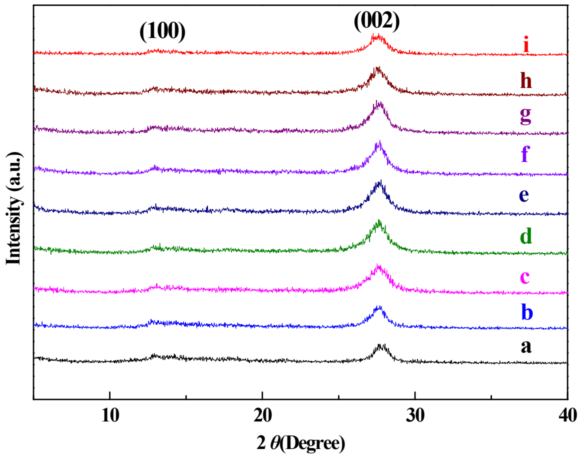


Fig. S1 XRD patterns of (a) pure g-C_3N_4, (b) 3%B-g-C_3N_4, (c) Rh/1%B-g-C_3N_4, (d) Rh/2%B-g-C_3N_4, (e) Rh/3%B-g-C_3N_4, (f) Rh/4%B-g-C_3N_4, (g) Rh/5%B-g-C_3N_4, (h) Rh/6%B-g-C_3N_4 and (i) Rh/g-C_3N_4.

S.3 FTIR spectra of the as-prepared samples

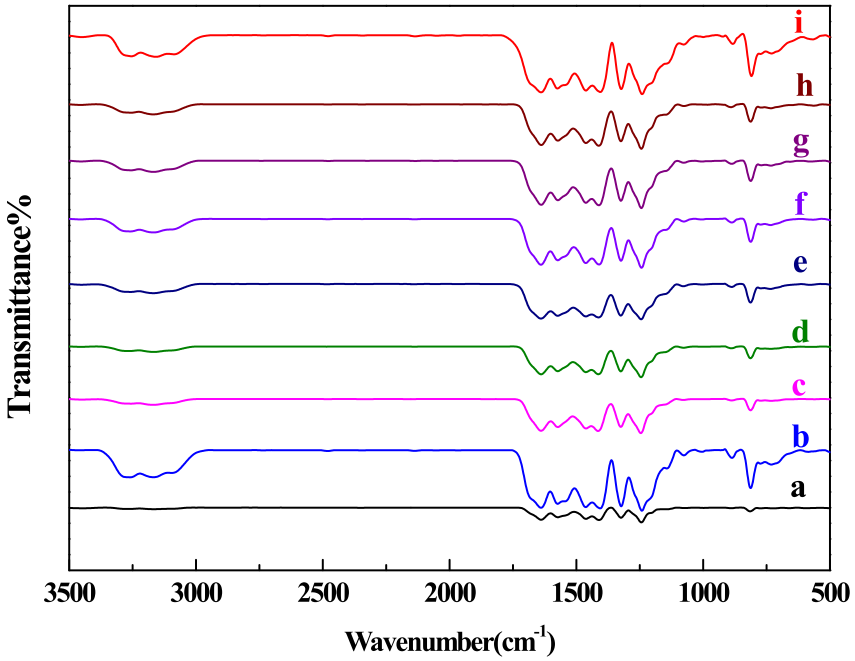


Fig. S2 FTIR spectra of (a) pure g-C_3N_4, (b) 3%B-g-C_3N_4, (c) Rh/1%B-g-C_3N_4, (d) Rh/2%B-g-C_3N_4, (e) Rh/3%B-g-C_3N_4, (f) Rh/4%B-g-C_3N_4, (g) Rh/5%B-g-C_3N_4, (h) Rh/6%B-g-C_3N_4 and (i) Rh/g-C_3N_4.

The functional groups and surface chemical species were revealed by the FTIR spectra of the pure g-C_3N_4, 3%B-g-C_3N_4, Rh/g-C_3N_4 and Rh/X%B-g-C_3N_4 samples in the Fig.S2. It can be clearly seen that pure g-C_3N_4, Rh/g-C_3N_4 and Rh/X%B-g-C_3N_4 exhibit almost the same IR features in the whole spectra. The broad and weak peaks in the range of 3000-3500 cm^{-1} are attributed to the adsorbed H_2O molecules and N-H vibration. The peaks in the region from 900 to 1800 cm^{-1} can be attributed to the stretching vibration of connected units of trigonal C-N(-C)-C (full condensation) or bridging C-NH-C units (partial condensation). The absorption band at 812 cm^{-1} originates from the bending mode of heptazine rings, indicating the existence of the basic melon units with NH/NH_2 groups. After the doped boron and deposited Rh nanoparticles on the surface of g-C_3N_4, all characteristic vibrational peaks related to g-C_3N_4 can also be found in the Rh/X%B-g-C_3N_4 materials, suggesting that the structural integrity of g-C_3N_4 remains intact.

S.4 SEM images of pure g-C_3N_4, 3%B-g-C_3N_4 and Rh/3%B-g-C_3N_4

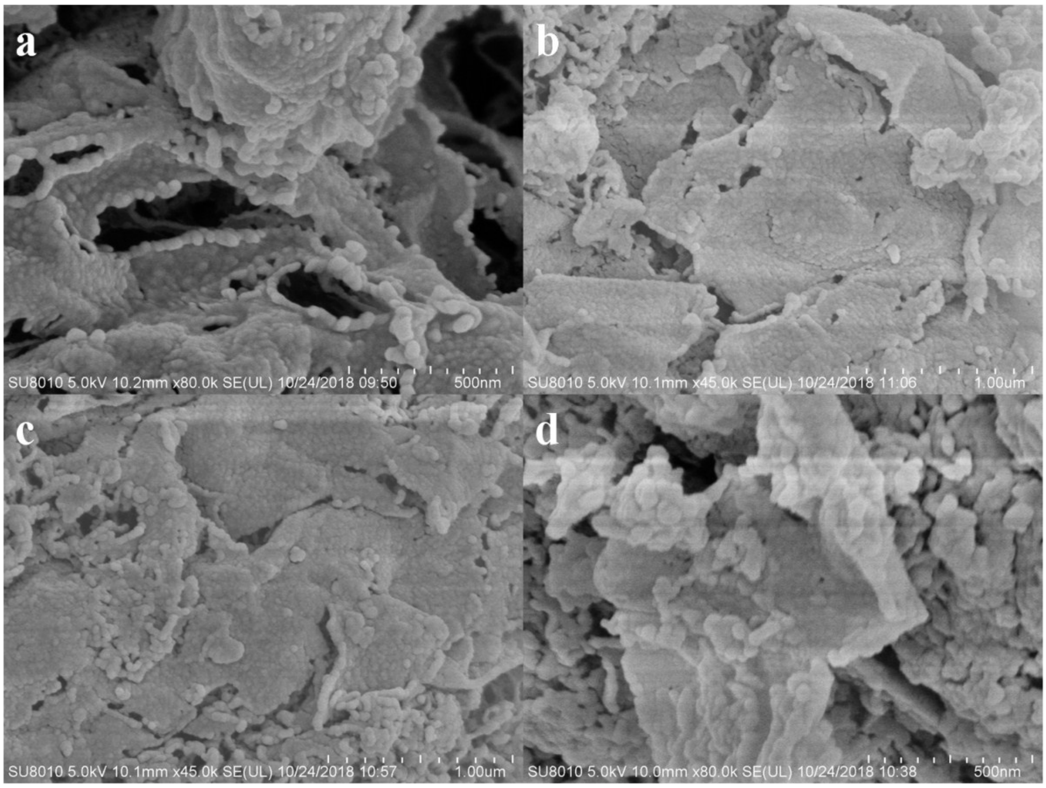


Fig. S3 SEM images of pure g-C_3N_4 (a), 3%B-g-C_3N_4 (b, c) and Rh/3%B-g-C_3N_4 (d).

S.5 Rh nanoparticles size distribution histograms of Rh/g-C_3N_4 and Rh/3%B-g-C_3N_4

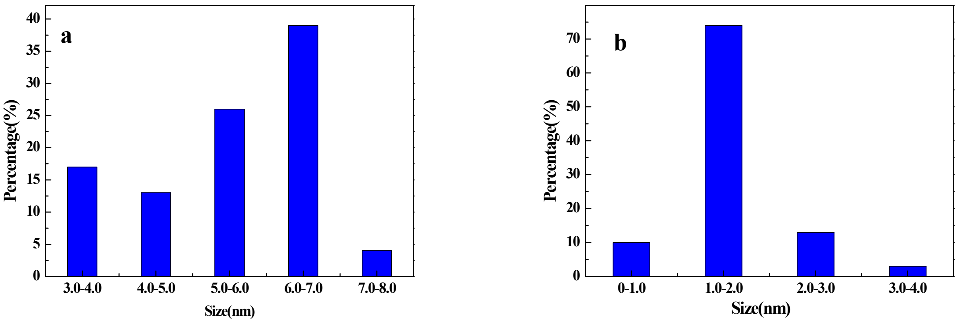


Fig.S4 Rh nanoparticles size distribution histograms of Rh/g-C_3N_4 (a) and Rh/3%B-g-C_3N_4 (b).

S.6 XPS spectrum of Rh/3%B-g-C_3N_4

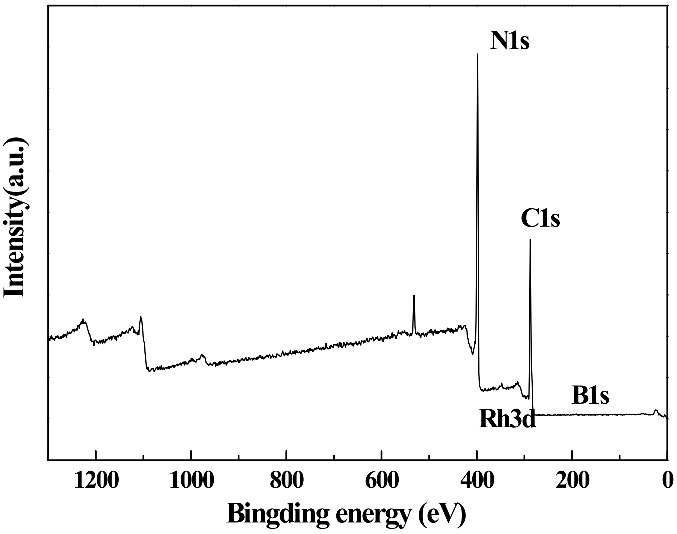


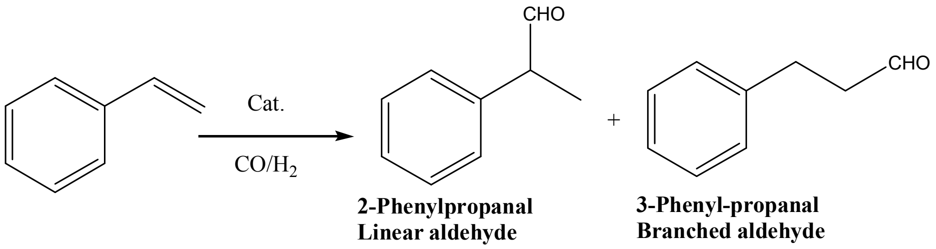
Fig. S5 XPS spectrum of Rh/3%B-g-C_3N_4

S.7 Textural properties of the pure g-C_3N_4 and Rh/X%B-g-C_3N_4

Table S1 Textural properties of the pure g-C_3N_4 and Rh/X%B-g-C_3N_4

Samples	g-C_3N_4	Rh/1%B-g-C_3N_4	Rh/2%B-g-C_3N_4	Rh/3%B-g-C_3N_4	Rh/4%B-g-C_3N_4	Rh/5%B-g-C_3N_4	Rh/6%B-g-C_3N_4
S_{BET} (m^2 g^{-1})	115.8	49.1	54.8	70.0	70.3	58.3	58.7

S.8 Scheme 2 Hydroformylation of styrene to linear and branched aldehydes



Scheme S2 Hydroformylation of styrene to linear and branched aldehydes followed by possible hydrogenation steps.

The catalytic capabilities of the Rh/g-C_3N_4 and Rh/X%B-g-C_3N_4 catalysts for the hydroformylation of alkenes were evaluated by using styrene as a model substrate to screen the optimized reaction conditions. Based on the catalytic cycle, linear and branched aldehydes can be produced from styrene as given in **Scheme S2**.

S9 Optimization of styrene hydroformylation catalyzed by Rh/3%B-g-C_3N_4

Table S2 Optimization of styrene hydroformylation catalyzed by Rh/3%B-g-C_3N_4 [a]

Entry	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (%)	TOF (h^{-1}) [b]	Selectivity (%) Aldehydes	Selectivity (%) B:L [c]
1	80	6.0	3	15.2	1800	100	74:26
2	90	6.0	3	59.3	7200	100	66:34
3	100	6.0	3	99.0	12000	100	57:43
4	100	5.0	3	94.6	11500	100	53:47
5	100	4.0	3	69.3	8400	100	50:50
6	100	6.0	2	82.7	10000	100	57:43
7	100	6.0	1	31.5	3800	100	59:41
8	100	6.0	0.5	18.8	2300	100	64:36

[a] Reaction conditions: Rh/3%B-g-C_3N_4: 0.01 g, toluene: 20 mL, styrene: 1.0 mL, [b] TOF = number of moles of product formed/(number of moles of Rh × time). [c] B : L = 2-phenylpropanal : 3-phenylpropanal.

A set of experiments were carried out to optimize the various reaction conditions such as effect of temperature, syngas (CO/H_2) pressure and reaction time on the hydroformylation of styrene using the same Rh/3%B-g-C_3N_4 catalyst. The results achieved are shown in Table S2. Temperature plays an important role in the hydroformylation performance of styrene using this catalytic system. As shown in entries 1-3, reaction carried out at 80 °C sees very low conversion of styrene. The

TOF of styrene is 1800 h^{-1} but the B/L ratio is as high as 74:26. At 90 ^{o}C, the TOF of styrene rises to 7200 h^{-1} while the B/L ratio decreases to 66:34 simultaneously. Continuously increasing the temperature to 100 °C increases the TOF to 12000 h^{-1} and the B/L ratio decreases to 57:43. Thus at high temperature in the tested range, more linear aldehydes are formed via hydroformylation of styrene. In a word, higher temperature would be helpful for increasing the TOF, but unfavorable for the B/L ratio. The optimum temperature at which good conversion (TOF =12000 h^{-1}) of styrene can achieve is found to be 100 ^{o}C.

The effect of syngas pressure on the reaction was studied (Table S2). In the range from 4.0 to 6.0 MPa, as shown in Table 2 (entries 3-5), the 69.3 % conversion of styrene and 50 % selectivity of branch aldehydes are achieved at 4.0 MPa. Upon increasing the syngas pressure to 6.0 MPa, higher conversion of styrene is afforded, though more branch aldehydes are also formed here too. Thus, the optimum pressure for this reaction is 6.0 MPa, furnished 99% conversion of styrene and 57 % selectivity of branch aldehydes.

Reaction time also affects the performance of catalysts in styrene hydroformylation. It is clear from the data in Table S2 that prolonged reaction time from 0.5 h to 3 h leads to an increase in styrene conversion from 18.8% to 99.0%, but the selectivity of branch aldehydes decreases from 64 % to 57 % (entries 4, 6-8). The optimum reaction time is 3 h.

S.10 Hydroformylation of various alkenes catalyzed by Rh/3%B-g-C_3N_4

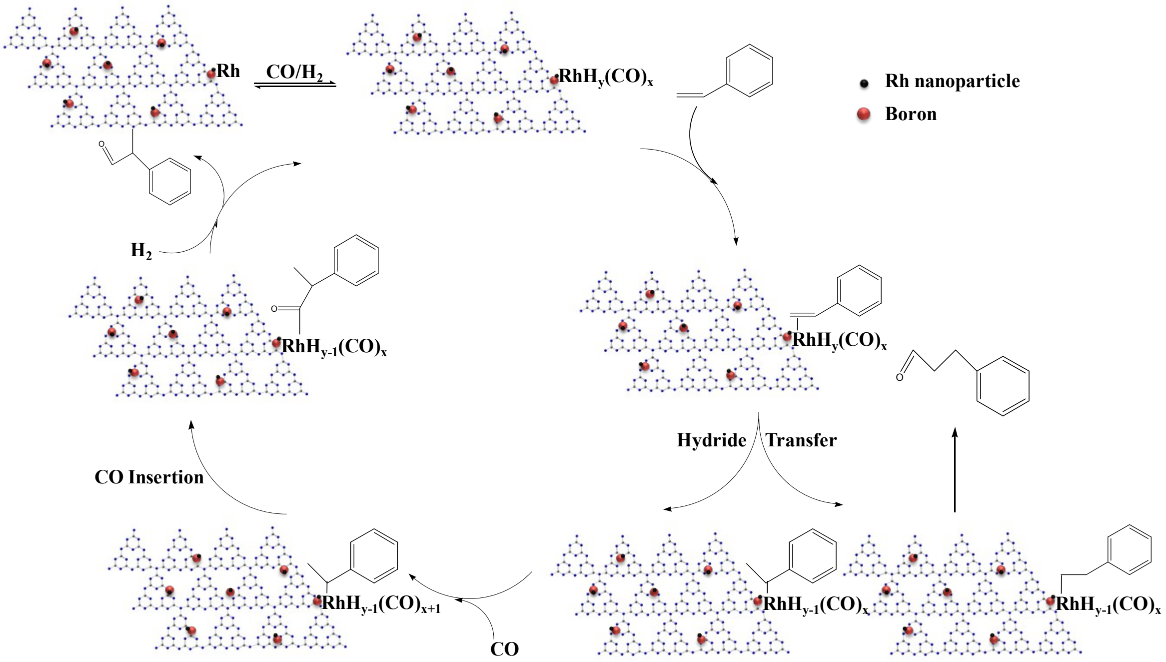
Table S3 Hydroformylation of various alkenes catalyzed by Rh/3%B-g-C_3N_4[a]

				Selectivity (%)	
Entry	Substrates	Conversion (%)	TOF (h^{-1}) [b]	Aldehydes	B:L [c]
1	styrene	99.0	12000	100	57:43
2	1-hexene	99.0	11100	86.7	49:51
3	1-octene	92.7	8200	88.3	51:49
4	cyclohexene [d]	57.3	7800	100	-

[a] Reaction conditions: Rh/3%B-g-C_3N_4: 0.01 g, toluene: 20 mL, substrates: 1.0 mL, reaction time: 3 h, Temp.: 100 °C, syngas(CO/H_2 =1): 6.0 MPa. [b] TOF = number of moles of product formed/(number of moles of Rh × time). [c] B : L = branched aldehyde : linear aldehyde. [d] Temp.: 120 °C

In order to examine the general applicability of Rh/3%B-g-C_3N_4 in hydroformylation of alkenes, various alkenes including 1-hexene, 1-octene and cyclohexene were used as substrates. Table S3 shows the results from the hydroformylation of various alkenes under the optimum reaction conditions. As expected, various alkenes are all hydroformylated with excellent conversion and selectivity toward the aldehyde products. No hydrogenation of alkenes to saturated alkanes is observed. In the hydroformylation of linear alkenes (entries 2 and 3), the conversion decreases with the increased chain length of the alkenes, which suggests that the coordination of the alkene in catalytic cycle becomes more difficult with the increase of alkene chain length.However, Rh/3%B-g-C_3N_4 is not effective and highly regioselective to produce linear aldehydes from these alkenes (Entries 1-3). For styrene, it can be due to π electron density on α carbon of styrene, which favors the attack of electropositive Rh metal, providing higher selectivity for branched aldehyde.[2] For 1-hexene and 1-octene, double bond shifted internal alkenes formed by isomerization are responsible for the high branched aldehyde selectivity.

S11. Proposed mechanism for Rh/B-g-C_3N_4 catalyzed hydroformylation of styrene



Scheme S3 Proposed mechanism for Rh/B-g-C_3N_4 catalyzed hydroformylation of styrene.

On the basis of the experimental results and previous literature [3-6], the plausible mechanism of the Rh/B-g-C_3N_4 catalyzed hydrformylation of styrene is shown in **Scheme S3**. When hydroformylation of styrene was conducted, the hydrogenation of styrene to ethylbenzene was not found in the experimental results. This result implied that the Rh/B-g-C_3N_4 catalyst was firstly activated by CO gas. Moreover, the Rh/B-g-

C_3N_4 catalyst was found mainly to be Rh (0) metal state from XPS spectra. Thus, the Rh (0) nanoparticles should be first to turn into $RhH_y(CO)_x$/B-g-C_3N_4 in the atmosphere of CO and H_2. Subsequence, the catalytic cycle involves successively the coordination of the styrene, the hydride transfer to provide the linear or branched alkyl species, CO coordination and migratory CO insertion, and then oxidative addition of H_2 followed by the reductive elimination of the aldehyde which regenerates the active species.

S.12 Effect of reaction medium on Rh/3%B-g-C_3N_4 catalyzed hydroformylation

Table S4 Effect of reaction medium on Rh/3%B-g-C_3N_4 catalyzed hydroformylation[a]

Entry	Solvent	Conversion (%)	TOF (h^{-1})[b]	Selectivity (%)	
				Aldehydes	B:L[c]
1	Toluene	99.0	12000	100	57:43
2	n-Heptane	97.95	11900	100	58:42
3	Alcohol	40.08	4900	100	58:42
4	DMF	-	-	-	-

[a] Reaction conditions: Rh/3%B-g-C_3N_4: 0.01 g, solvent: 20 mL, styrene: 1.0 mL, reaction time: 3 h, Temp.: 100 °C, syngas(CO/H_2 =1): 6.0 MPa. [b] TOF = number of moles of product formed/(number of moles of Rh ×time). [c] B : L = 2-phenylpropanal : 3-phenylpropanal.

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