Short communication

PPh₃ functionalized Rh/rGO catalyst for heterogeneous hydroformylation: Bifunctional reduction of graphene oxide by organic ligand

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GRAPHICAL ABSTRACT
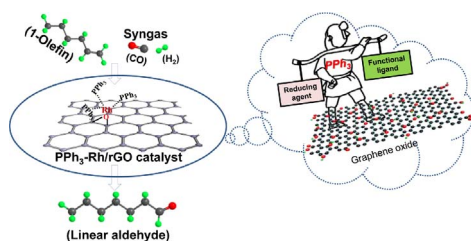
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ABSTRACT

Designing catalyst with the combined merits of heterogeneous catalysts and homogeneous catalysts through much simple one-step preparation process is always a challenge in catalysis. In this report, organic ligand triphenylphosphine (PPh₃) is first introduced as a reducing agent to reduce graphene oxide (GO) and accomplish a reduced graphene oxide (rGO) supported metal-ligand complex catalyst simultaneously. Here, the employed PPh₃ not only acts as an effective reducing agent to reduce GO, but also as a functional group to in-situ form ligand functionalized rhodium catalyst immobilized on rGO (PPh₃-Rh/rGO). The prepared PPh₃-Rh/rGO catalyst, as a heterogeneous catalyst, is applied in 1-olefins hydroformylation to form normal aldehyde, exhibiting remarkable catalytic activity and selectivity compared with other heterogeneous catalysts. It affords aldehydes in higher yields with better regioselectivity on linear products than those of other two reference catalysts reduced by ethylene glycol and hydrazine hydrate. More importantly, this efficient and simple method for preparing ligand modified metal complex catalyst supported on rGO is scalable. The great varieties of organic ligands can be chosen to extend the synthetic strategy for preparing rGO supported metal-ligand complex catalysts for various reactions.

1. Introduction

Homogeneous catalysts can realize high activity and selectivity for synthesizing fine chemical products, but their separation from the products remains a great challenge and limits their industrial application [1–4]. Therefore, the heterogenization or immobilization of homogeneous catalysts onto the solid supports have aroused considerable concerns in recent years [5–9]. Rhodium based homogeneous

catalysts are the most efficient catalysts under mild conditions for hydroformylation of olefins, one of the largest homogeneously catalyzed reactions to produce aldehydes in industry [10]. In order to overcome the drawbacks of homogeneous catalyst, many efforts have been done to develop Rh based heterogeneous catalysts for hydroformylation reaction. Homogeneous species chemically grafted on the solid silica has been investigated for heterogeneous hydroformylation [11]. Heterogenizations of homogeneous catalysts in aqueous phase, ionic liquids or fluorous phase have also been employed for hydroformylation in biphasic systems [12–14]. These catalysts can be readily separated and recycled from the reaction mixtures, but the synthesis procedures and operating conditions are usually complicated. Thus, it is highly necessary to exploit solid supported rhodium catalysts with high activity by simple preparation methods. Recently, Zhao and Yang et al. adopted surface modified mesoporous silica nanospheres as stabilizer to support Rh-TPPTS, forming an efficient and stable oil/water Pickering emulsion system, which exhibited excellent performance for hydroformylation of 1-octene [15]. Xiao and Ding et al. prepared porous organic polymers by copolymerized vinyl functionalized ligands to support Rh species, which demonstrated excellent activity and selectivity [16,17]. In our previous study, graphene supported Rh nanoparticles prepared by one-pot reduction method, exhibited outstanding activity and selectivity in comparison to activated carbon or CNTs based Rh catalysts, making graphene an intriguing support for metal catalysts [18].

Graphene, a new class of carbon materials, has attracted considerable attentions and acquired fast-paced development because of its unique properties [19,20]. Due to its high thermal, chemical and mechanical stabilities, as well as high surface area, graphene is regarded as an ideal catalyst support for heterogeneous catalyst [21–24]. Benefitting from the rich surface properties, graphene also has the potential to promote the catalytic activity and stability of the supported species through cation-π interactions or π-π stacking [25,26]. Moreover, the desirable 2D support layers of graphene are beneficial to the diffusion of reactants and products. Chemical reduction of graphene oxide (GO) is an effective and convenient approach to prepare reduced graphene oxide (rGO) [27–30]. Furthermore, the rGO prepared by chemical reduction method owns some surface defects, which are beneficial to improve the catalyst activity if it is employed as the heterogeneous catalyst support. Until now, a wide range of reducing agents, such as borohydrides ($NaBH_4$), nitrogen-containing reducing agents (hydrazine, urea, ammonia), oxygen-containing reducing agents (alcohol, L-ascorbic acid) and so on [27,28,30–34], have been utilized to reduce GO to rGO. However, these reducing agents only have reduction role, and excessive reducing agents employed for GO reduction usually result in the contamination of the resultant product [21,27,35]. Therefore, a reducing agent with the function for GO reduction coupled with being acted as promoter to boost the catalyst performance is an ideal methodology in the research of reduction and functionalization of graphene for specific applications.

Organic ligands are extremely important in homogeneous catalysis. Triphenylphosphine (PPh_3) as a common and relatively inexpensive organophosphorus ligand has been widely utilized in the fabrication of ligands-metal complexes for homogeneous catalysis [36,37]. Nevertheless, the difficulty of separation and recovery severely limits their applications. In order to overcome the difficulties of catalyst separation and recovery in homogeneous catalysis, many efforts have been undertaken by developing the corresponding heterogeneous catalysts. Heterogenization or immobilization of these homogeneous complexes onto solid supports is regarded as an effective method. Because of large specific surface area and high adsorption capacity, graphene and its derivatives (such as GO) can be valuable supports to interact with various species. In homogeneous catalysis system, the usage of PPh_3 mainly depends on its nucleophilicity and reducibility, as well as excellent metal coordination-chelation ability with transition metals [36,38]. These virtues of PPh_3 also provide us a new perspective on the reduction of rGO by PPh_3, along with in-situ formation of ligand

functionalized transition metal catalyst supported on rGO.

Herein, the organic ligand of PPh_3 was first employed to reduce GO and in situ prepare rGO supported metal-ligand catalyst. With our design, PPh_3 acts as not only a reducing agent, but also a functional group to modify Rh on rGO. GO sheets mixed with metal precursor ($RhCl_3$) were simultaneously reduced to obtain PPh_3 functionalized Rh/rGO heterogeneous catalyst (PPh_3-Rh/rGO) facilely. The PPh_3-Rh/rGO catalyst, anchoring homogeneous ligand-metal on the heterogeneous rGO, exhibited excellent catalytic activity and product selectivity in hydroformylation of 1-olefins, as well as easy separation and recycle.

2. Experimental

2.1. Preparation of catalysts

The PPh_3-Rh/rGO catalyst was prepared via a one-pot liquid phase reduction method (Fig. S1). 0.3 g of graphite oxide prepared from natural graphite by modified Hummer's method (Supplementary Material) was firstly dispersed in 150 mL ethanol, and then homogeneous colloidal suspension of GO was achieved after ultrasonic treatment for 2 h. 0.008 g $RhCl_3 \cdot 3H_2O$ was added into the above suspension and stirred for 10 min. After added 0.5 g PPh_3, the mixed suspension was shaken vigorously in glove box under nitrogen atmosphere. Subsequently, the mixture was heated in oil bath at 90 °C for 6 h with stirring and water reflux under nitrogen protection. Finally, the mixture was filtered immediately and repeatedly rinsed by hot ethanol to remove the generated triphenylphosphine oxide ($O=PPh_3$) and dissociative PPh_3. The obtained sample was dried in vacuum at 60 °C for 24 h to get PPh_3-Rh/rGO catalyst.

Ethylene glycol (EG) and hydrazine hydrate ($N_2H_4 \cdot H_2O$) were also utilized to prepare Rh/rGO catalysts as reference catalysts: EG-Rh/rGO and N_2H_4-Rh/rGO. The preparation methods were described in Supplementary Material.

2.2. Characterization of catalysts

Detailed descriptions of catalysts characterizations were given in Supplementary Material.

2.3. Catalytic activity test

The reaction of 1-olefin hydroformylation was carried out in a stainless steel autoclave. The reaction details were shown in Supplementary Material. The liquid products were analyzed quantitatively with a gas chromatograph (Shimadzu GC 2014) equipped with a capillary column (InertCap 5, length: 30 m) and a flame ionization detector (FID).

3. Results and discussion

3.1. The reduction of GO by PPh_3

The reduction effect of PPh_3 on GO was characterized by X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS). In order to prove that GO was indeed reduced by PPh_3, instead of other factors (such as temperature or solution), Rh/GO was also prepared by the same preparation method without using PPh_3. Fig. 1A compares the XRD patterns of graphite oxide, Rh/GO and PPh_3-Rh/rGO. For graphite oxide, the obvious peak located at 10.7° is the characteristic of graphite oxide [39]. Due to the reduction of GO to rGO by PPh_3, the peak at 10.7° disappears and two peaks at 24° and 43° belonging to the crystalline structure of rGO appear on PPh_3-Rh/rGO [18]. In contrary, the peak at 10.7° is still observed on Rh/GO, indicating that the GO sheets aggregate and reassemble to graphite oxide without reduction by PPh_3. The SEM image of Rh/GO (Fig. 1B, top) shows the agglomeration of exfoliated sheets, while that of PPh_3-Rh/rGO (Fig. 1B, bottom) mainly
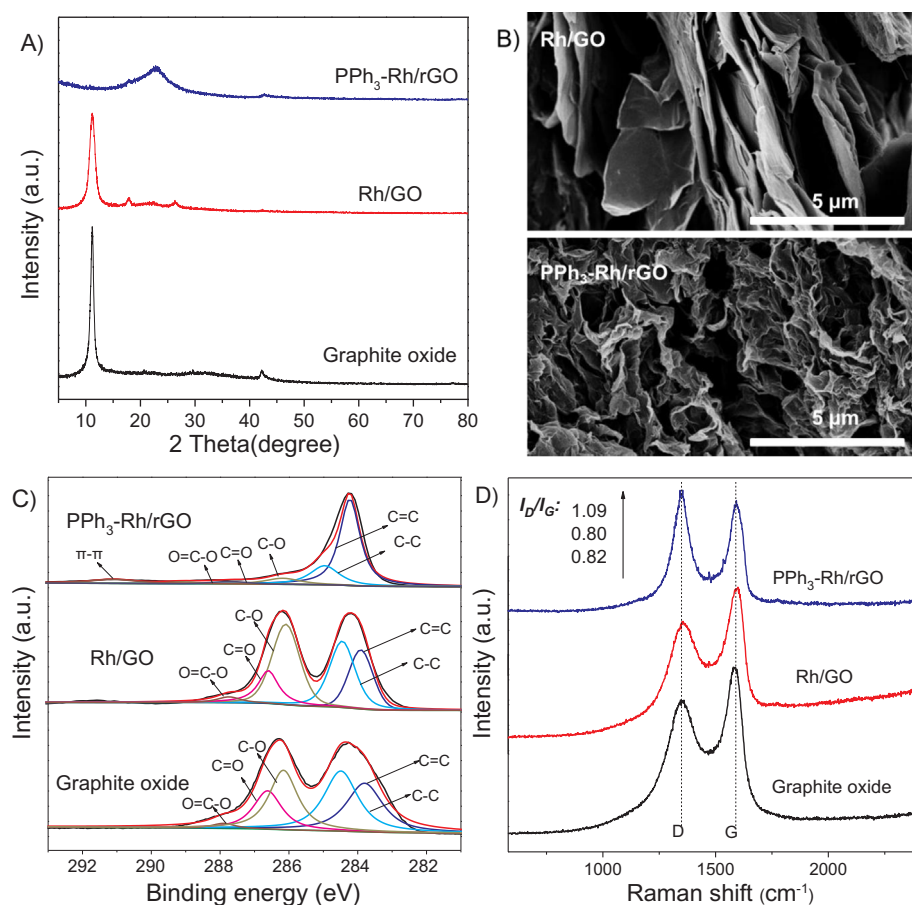
Fig. 1. (A) XRD patterns of graphite oxide, Rh/GO and PPh$_3$-Rh/rGO; (B) SEM images of Rh/GO and PPh$_3$-Rh/rGO; (C) C1s XPS spectra of graphite oxide, Rh/GO and PPh$_3$-Rh/rGO; (D) Raman spectra of graphite oxide, Rh/GO and PPh$_3$-Rh/rGO.

presents seldom aggregated and more ultrathin graphene sheets. Furthermore, the specific surface area of PPh$_3$-Rh/rGO obtained from N$_2$ adsorption-desorption isotherm (Fig. S2) reaches 424.3 m^2/g, much larger than 31.7 m^2/g of Rh/GO. The reduction of GO to rGO by PPh$_3$ was also confirmed by XPS. As shown in Fig. 1C, the fitted C1s suggests that the intensities of C—O (at 286.8 eV), C=O (at 287.2 eV) and O—C=O (at 288.4 eV) on PPh$_3$-Rh/rGO catalyst decrease significantly compared to those of GO and Rh/GO, revealing the successful reduction of GO by PPh$_3$ [30]. Raman spectroscopy is an effective characterization method for carbon material [40]. The I$_D$/I$_G$ value of PPh$_3$-Rh/rGO is obviously larger than those of graphite oxide and Rh/GO as shown in Fig. 1D, indicating more defects emerged on PPh$_3$-Rh/rGO due to the reduction by PPh$_3$ [41].

These findings indicate that PPh$_3$ is an effective reducing agent to reduce GO to rGO. The reducing action of PPh$_3$ is driven from the formation of O=PPh$_3$ which removes the oxygen from GO to form rGO [38], as illustrated the schematic in Fig. 2A. Furthermore, the role of temperature in reduction of GO by PPh$_3$ is also investigated. When the reduction temperature is 80 °C, GO cannot be well reduced by PPh$_3$ as proved by XPS (Fig. 2B). PPh$_3$ can act as a better reducing agent at a higher temperature (> 80 °C), because the formation of O=PPh$_3$ is thermodynamically favored at higher temperature [38].

3.2. The functional action of PPh$_3$ on Rh/rGO

PPh$_3$ plays as not only an effective reducing agent to reduce GO, but also a functional group to in-situ form ligand functionalized Rh catalyst immobilized by rGO. The functional action of PPh$_3$ on Rh/rGO can be identified by XPS. As shown in Fig. 3A, in addition to the peaks of C1s, O1s and Rh3d, two peaks of Cl2p and P2p exist on PPh$_3$-Rh/rGO, in comparison to Rh/GO. According to the XPS result of PPh$_3$-Rh/rGO, the

mole ratio of P to Rh is about 4.5. The binding energies of these peaks (Rh3d$_{3/2}$ at 309.4 eV, Cl2p at 189.5 eV, and P2p at 131.8 eV) given in Fig. 3B–D are similar to those of RhCl(PPh$_3$)$_x$, which proves the formation of PPh$_3$-Rh complex on rGO [42–44]. Further evidence for the formation of PPh$_3$-Rh complex on rGO can be obtained by solid-state ^{31}P NMR spectrum of PPh$_3$-Rh/rGO catalyst to verify the coordination between PPh$_3$ and Rh in Fig. 4. The ^{31}P NMR spectrum displays two main peaks at −5.15 and 31.16 ppm. The sharp peak at −5.15 ppm is assigned to the free PPh$_3$ adsorbed on rGO [45]. The peak at 31.16 ppm overlapped with a weak peak at 26.01 ppm is attributed to the PPh$_3$ coordinated with Rh indicating the in situ formation of PPh$_3$-Rh complex on rGO [46].

The distribution of Rh and P on the surface of rGO can be determined by STEM-EDS mapping and HRTEM (Fig. 5). From the STEM-EDS element mapping in Fig. 5A–D, we can see that both P and Rh are highly dispersed on rGO. However, no Rh nanoparticles are detected from HRTEM images (Fig. 5E and F), excluding the formation of Rh nanoparticles. The result indicates PPh$_3$ functionalized Rh catalyst, as a homogeneous catalysts, is immobilized on rGO.

Thermogravimetric measurement of PPh$_3$-Rh/rGO in nitrogen (Fig. S3) discloses that the weight begins to loss above 250 °C, which can be attributed to the decomposition of PPh$_3$-Rh complex on rGO, demonstrating that PPh$_3$-Rh/rGO catalyst has good thermal stability. The TGA of PPh3-Rh/rGO in air (Fig. S4) was also conducted to obtain the Rh loading 2.72%).

3.3. Catalytic performance of various catalysts

Hydroformylation reaction, i.e. adding H$_2$ and CO to the C=C bond of 1-olefins with 100% atomic economy to yield aldehydes or alcohols, is an important catalysis process [10]. Hydroformylation of long-chain
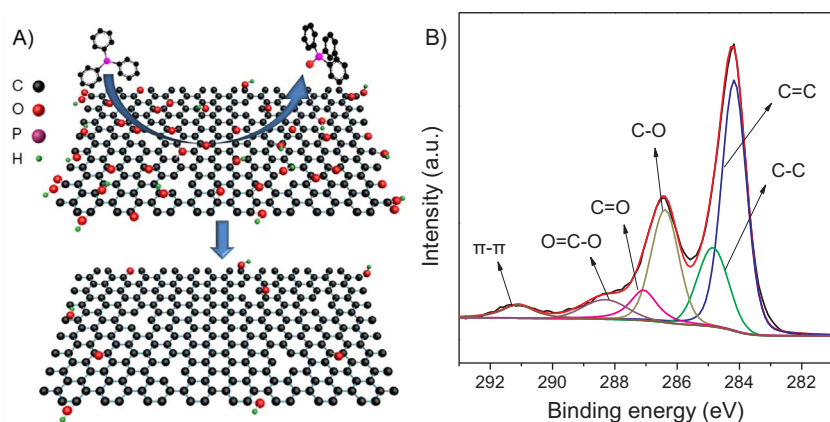
Fig. 2. (A) Schematic of graphene oxide reduced by PPh_3; (B) C1s XPS spectra of graphene oxide reduced by PPh_3 at 80 °C.

olefins to produce aliphatic aldehydes is of great value because of their high industrial application in the production of detergents, plasticizers, solvents and surfactants [47–49]. The catalytic performance of as-designed PPh_3-Rh/rGO catalyst for olefins hydroformylation was evaluated by employing 1-hexene and 1-octene as model substrates in this report.

In order to clarify the roles of PPh_3 as reducing agent and functional ligand for PPh_3-Rh/rGO, other two reducing agents, ethylene glycol (EG) and hydrazine hydrate ($N_2H_4 \cdot H_2O$) were utilized to prepare Rh/rGO catalysts: EG-Rh/rGO and N_2H_4-Rh/rGO (Figs. S5–S11). Different form PPh_3-Rh/rGO catalyst, Rh nanoparticles were formed on rGO with the reduction action of EG and N_2H_4 as shown in TEM images (Figs. S5). The rGO supported Rh nanoparticles catalyst exhibited high catalytic activity for hydroformylation in previous work [18]. Tables 1 and S1 present the catalytic performance of various catalysts on the hydroformylation of 1-hexene or 1-octene. EG and $N_2H_4 \cdot H_2O$, as two conventional reducing agents for graphene oxide reduction, were often
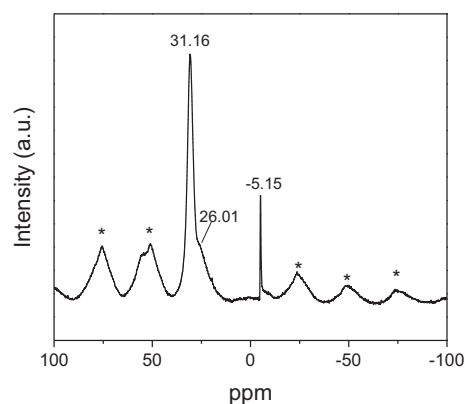

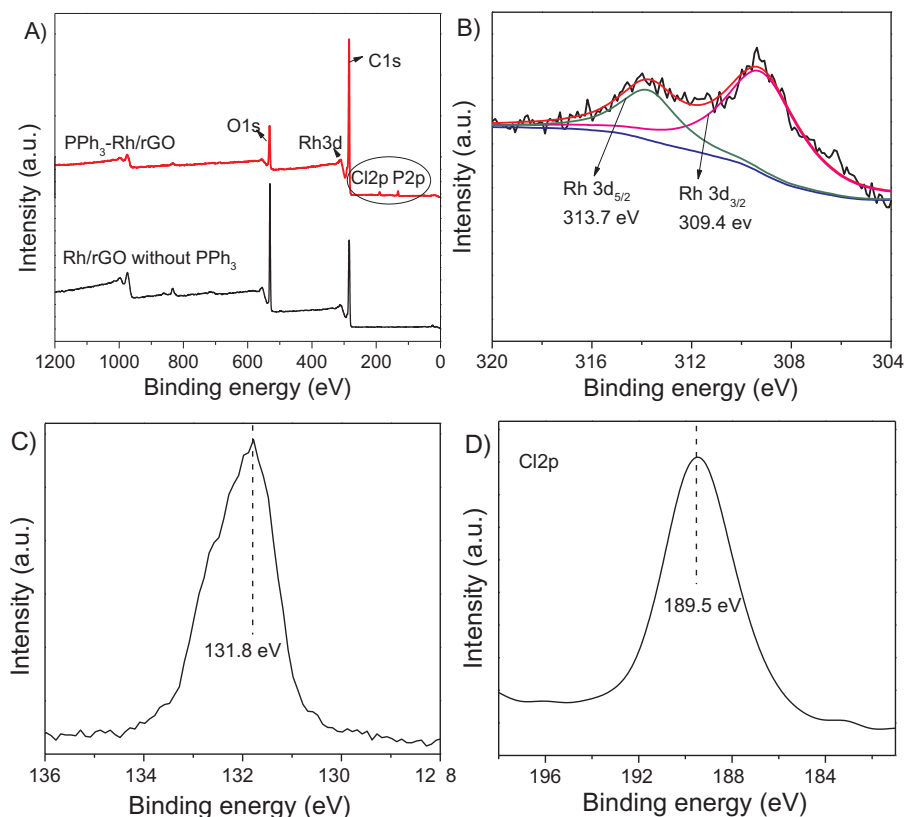**Fig. 4.** ^{31}P NPR spectrum of PPh_3-Rh/rGO catalyst.

Fig. 3. (A) XPS survey spectra of Rh/GO and PPh_3-Rh/rGO; (B) Rh3d, (C) P2p and (D) Cl2p spectra of PPh_3-Rh/rGO.
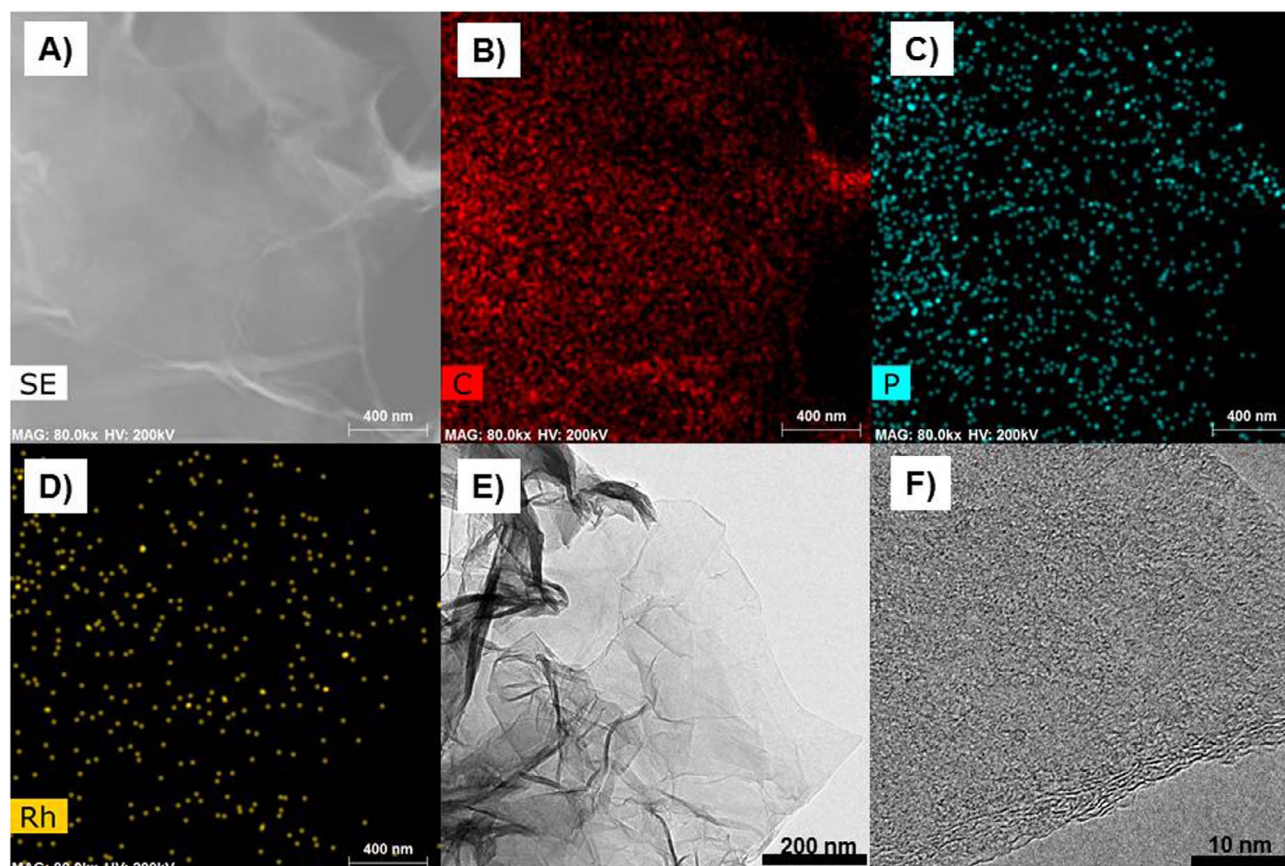
Fig. 5. STEM-EDS element mappings and TEM images of PPh$_3$-Rh/rGO catalyst: (A) STEM image; (B) C element mapping; (C) P element mapping; and (D) Rh element mapping; (E) TEM image at low magnification; (F) TEM image at high magnification.

Table 1
Catalytic performance of varied catalysts for hydroformylation of 1-hexene and 1-octene.[a]

No.	Catalyst	Reactant	Conv. (%)[b]	Yield (%)[c]	n/i[d]
1	PPh$_3$-Rh/rGO	1-Hexene	99.9	99.2	2.10
2[e]	PPh$_3$-Rh/rGO	1-Hexene	99.4	98.9	2.06
3	EG-Rh/rGO	1-Hexene	99.5	82.7	0.90
4	N$_2$H$_4$-Rh/rGO	1-Hexene	99.4	77.7	1.00
5	PPh$_3$-Rh/rGO	1-Octene	99.9	99.0	1.46
6	EG-Rh/rGO	1-Octene	99.9	92.3	0.67
7	N$_2$H$_4$-Rh/rGO	1-Octene	99.7	77.6	0.81

[a] Reaction conditions: 0.10 g catalyst, 3.73 g 1-hexene or 4.97 g 1-octene, 5 MPa syngas (CO/H$_2$ = 1), 90 °C, 4 h.
[b] The conversion of 1-hexene or 1-octene.
[c] The yield of aldehyde.
[d] n/i ratio of aldehyde.
[e] Reuse.

used to prepare rGO supported metal catalyst for various reactions. In our work, both reference catalysts of EG-Rh/rGO and N$_2$H$_4$-Rh/rGO catalysts show high catalytic activity for olefins conversion, but with lower aldehyde selectivity. PPh$_3$-Rh/rGO catalyst exhibits both higher catalytic activity and better yield of aldehyde than EG-Rh/rGO and N$_2$H$_4$-Rh/rGO catalysts. More importantly, PPh$_3$-Rh/rGO not only gives higher yield of aldehydes, but also exhibits excellent regioselectivity of linear aldehydes. No matter 1-hexene or 1-octene is selected as the substrate, the n/i ratios (molar ratio of linear to branched aldehydes)

obtained by PPh$_3$-Rh/rGO catalyst are rather higher than those obtained by reference catalysts. For EG-Rh/rGO and N$_2$H$_4$-Rh/rGO catalysts, adding PPh$_3$ could also improve their catalytic performance as shown in Table S2. The yield and n/i ratio of aldehyde can be both increased by adding PPh$_3$. It indicated that PPh$_3$ plays an important effect for promoting hydroformylation. Nonetheless, even adding PPh$_3$, the catalytic performances of EG-Rh/rGO and N$_2$H$_4$-Rh/rGO catalysts are still lower than that of PPh$_3$-Rh/rGO. The excellent catalytic performance of PPh$_3$-Rh/rGO should be attributed to the anchored PPh$_3$ ligands coordinated to Rh highly dispersed on rGO, as shown in Fig. 6. Different from these reducing agents (EG and N$_2$H$_4$·H$_2$O) with only single reducing function, excessive PPh$_3$ can also act as a functional ligand coordinated to Rh, besides its function as reducing agent. The steric and electronic attributes of these ligands coordinated to the Rh are in favour of improving the regioselectivity of linear aldehydes in olefins hydroformylation reaction, which therefore leads to the higher n/i ratio of aldehydes for PPh$_3$-Rh/rGO catalyst [17,50,51]. Moreover, different from the traditional homogeneous metal-ligand catalysts for hydroformylation, the PPh$_3$-Rh/rGO catalyst can be separated and recycled easily. The reused PPh$_3$-Rh/rGO catalyst can keep high catalytic activity and selectivity as the fresh one, as given in Table 1. Otherwise, the liquid separated from the catalyst after first cycle and added into 5 mL 1-hexene to react under the same reaction conditions but no activity was detected. The recycling of PPh$_3$-Rh/rGO catalyst for hydroformylation of 1-hexene was tested though five cycles under the same reaction conditions. The high 1-hexene conversion and products selectivity of the repeated catalyst are maintained after 5 cycles, as shown in Fig. S12.
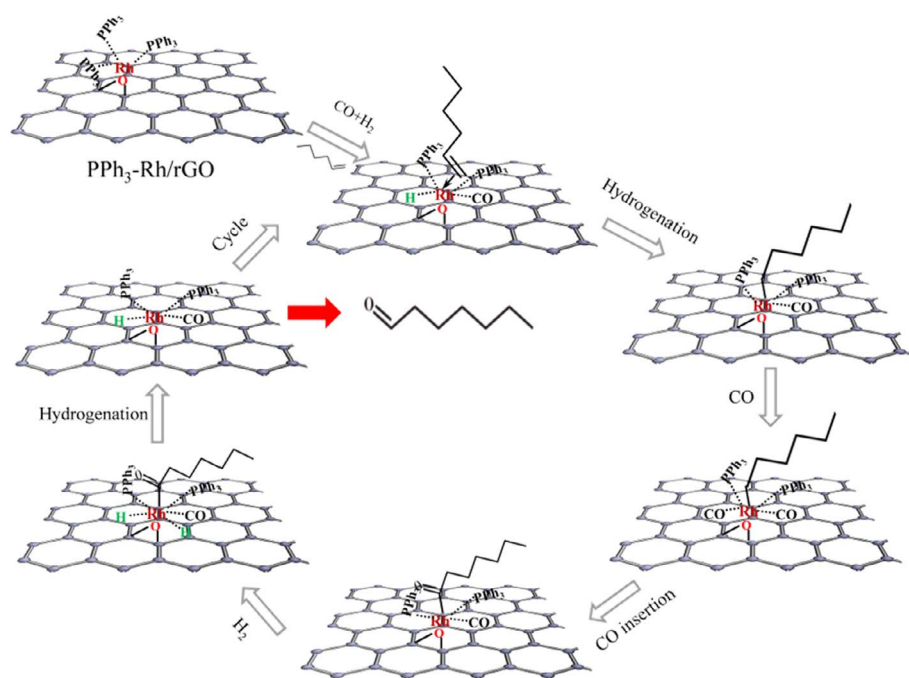
Fig. 6. Schematic of 1-hexene hydroformylation.

4. Conclusions

In summary, an organic ligand of PPh_3 was first used as reducing agent to reduce GO and as functional group to fabricate PPh_3 functionalized Rh/rGO heterogeneous catalyst simultaneously. The as-made PPh_3-Rh/rGO catalyst is an efficient heterogeneous catalyst for 1-olefins hydroformylation exhibiting excellent catalytic performance, not only enhancing aldehyde yield, but also improving linear aldehyde selectivity and the n/i ratio in the final products. This contribution, for the first time, demonstrates an organic ligand of PPh_3 as multifunctional reducing agent for both reducing GO to form rGO and synthesizing PPh_3 modified metal complex catalyst supported on rGO. The presented catalyst preparation method makes the immobilization of homogeneous ligand catalysts on the solid support easily. The great varieties of organic ligands can be chosen appropriately to extend the synthetic strategy for preparing rGO supported catalysts for various reactions. The research results also provide a new viewpoint for extending the selection of reducing agent to synthesize graphene-based materials for special applications.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.08.023.

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