PPh_3 functionalized Rh/rGO catalyst for heterogeneous hydroformylation: Bifunctional reduction of graphene oxide by organic ligand

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Abstract: Organic ligand triphenylphosphine (PPh_3) is first introduced to reduce graphene oxide (GO) and accomplish a reduced graphene oxide (rGO) supported metal-ligand complex catalyst simultaneously. It acts as both reducing agents and a functional group to in-situ form ligand functionalized rhodium catalyst immobilized on rGO. The heterogeneous PPh_3-Rh/rGO catalyst is applied in 1-olefins hydroformylation to form normal aldehyde, exhibiting remarkable activity and selectivity. It affords aldehydes in higher yields with better regioselectivity on linear products and it is scalable. Many organic ligands can be chosen to extend the synthetic strategy for preparing rGO supported metal-ligand complex catalysts for various reactions.

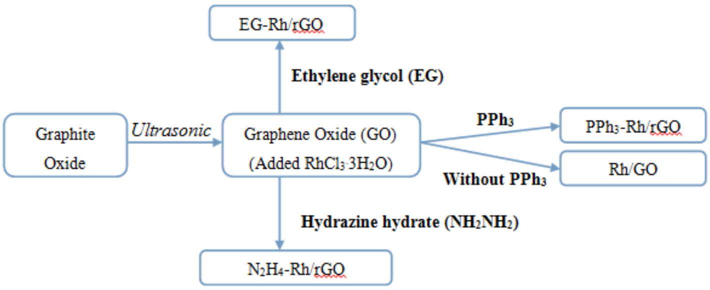
Keywords: Reduced graphene oxide, Bifunctional reducing agent, Triphenylphosphine.

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 has aroused considerable concerns in recent years. 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

The PPh_3-Rh/rGO catalyst was prepared via a one-pot liquid phase reduction method (Scheme 1). 0.3 g of graphite oxide prepared from natural graphite by modified Hummer's method 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.

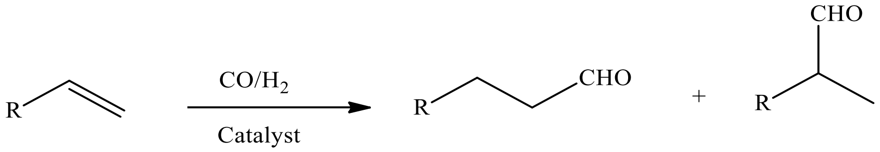


Scheme 1. Illustration of the preparation process of catalysts

3. Results and discussion

Tables 1 presents 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 used to prepare rGO supported metal catalyst for various reactions. In our work, both reference catalysts of EG-Rh/rGO and N_2H_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_2H_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_2H_4-Rh/rGO catalysts, adding PPh_3 could also improve their catalytic performance. The yield and n/i ratio of aldehyde can be both increased by adding PPh_3. It indicates that PPh_3 plays an important effect for promoting hydroformylation.

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_2H_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_2H_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.

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.

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