CJC Chinese Journal of Chemistry
中国化学 - An International Journal

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This work may now be cited as: *Chin. J. Chem.* **2019**, *37,* 10.1002/cjoc.201900427.

WILEY-VCH SIOC CCS

ISSN 1001-604X • CN 31-1547/O6
mc.manuscriptcentral.com/cjoc
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Organic ligand-free hydroformylation with Rh particles as catalyst

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Cite this paper: *Chin. J. Chem.* **2019**, *37*, XXX—XXX. **DOI: 10.1002/cjoc.201900XXX**

Summary of main observation and conclusion An efficient and organic ligand-free heterogeneous catalytic system for hydroformylation of olefins is highly desirable for both academy and industry. In this study, simple Rh black was employed as a heterogeneous catalyst for hydroformylation of olefins in the absence of organic ligand. The Rh black catalyst showed good catalytic activity for a broad substrate scope including the aliphatic and aromatic olefins, affording the desired aldehydes in good yields. Taking the hydroformylation of ethylene as an example, 86% yield of propanal and TOF of 200 h^{-1} were obtained, which was superior to the reported homogeneous catalytic systems. In addition, the catalyst could be reused five times without loss of activity under identical reaction conditions, and the Rh leaching was negligible after each cycle.

Background and Originality Content

Hydroformylation is the addition of olefins and synthesis gas in the presence of a catalyst for the formation of aldehydes and was discovered in early 1938 by Otto Roelen, which represents one of the largest homogeneously catalyzed reactions in industry today and has more than 10 million metric tons of oxo chemicals annually. [1-5] The aldehyde can be extensively served as key intermediates in the synthesis of esters, alcohols, carboxylic acids and other fine chemicals, which are used for the manufacturing of plasticizers, surfactants, soaps, and detergents. [6-8]

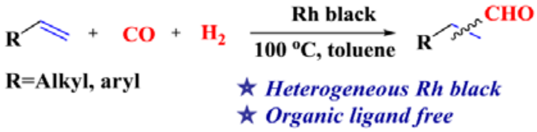
Over the past years, both industry and academia have invested heavily in research related to hydroformylation, [9] and a number of transition metals, such as Rh, [10-12] Co, [13-15] Ir, [16-19] Ru, [20-22] Pt [23-29] and Pd [30-32] have been used for catalyze olefins hydroformylation reaction. Much effort has been focused on the use of Rh complexes as catalysts, due to their better activity and selectivity in the hydroformylation of olefins than heterogeneous [6, 33] However, the separation and recovery is important technical problems for the soluble catalysts.

Then, it is highly desirable to develop heterogeneous Rh-based catalysts. And up to now, Rh supported on many solid supports, such as SiO_2, [34-36] Cu_2O, [37] ZnO, [38] carbon materials, [39-43] TiO_2, [44] and Al_2O_3, [45, 46] have been investigated for heterogeneous olefins hydroformylation. Nevertheless, the activity and selectivity are usually lower compared with the corresponding homogeneous catalysts. So it is still extremely relevant to search for new catalytic systems that effectively combine the advantages of both heterogeneous and homogeneous catalysis in the context of widening the range of applications of hydroformylation in fine chemistry industrial processes.

One of the main synthetic strategies for achieving these goals is based on the development of heterogenization of homogeneous catalysts, which usually tethers metal complexes to either organic polymers or inorganic matrixes modified with organic phosphine ligands. [47-65] This strategy allows not only their easy separation/reutilization but also the potential enhancement of activity and selectivity. However, the use of expensive and sensitive organic phosphine ligand as well as the complicated processes for homogeneous catalysts immobilized on support limited the further application.

In the current work, an efficient organic ligand-free heterogeneous catalytic system for hydroformylation of olefins was constructed with simple Rh particles as the catalyst. The catalyst system exhibited excellent catalytic activity in hydroformylation of olefins, as well as easy separation and recycle.

Scheme 1 Organic ligand-free heterogeneous Rh-based catalytic system for hydroformylation of olefins.



Results and Discussion

Characterization of catalysts

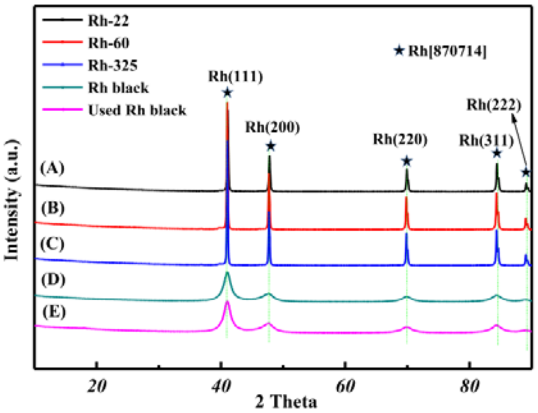


Figure 1 XRD pattern of catalysts. (A) Rh-22 mesh; (B) Rh-60 mesh; (C) Rh-325 mesh; (D) Rh black. (E) Reused five times Rh black.

The Rh particle catalysts were characterized by XRD, XPS, SEM, TEM and N_2 adsorption-desorption to explore the correlation of the structure and activity. The XRD patterns of Rh-22, Rh-60, Rh-325, Rh black and used Rh black catalysts are compared in Figure 1. The diffraction pattern of Rh particles shows five peaks at about 41.1°, 47.8°, 69.9°, 84.4° and 89.1°, which can be ascribed to the (111), (200), (220), (311) and (222) reflections of Rh (JCPDS no. 870714).

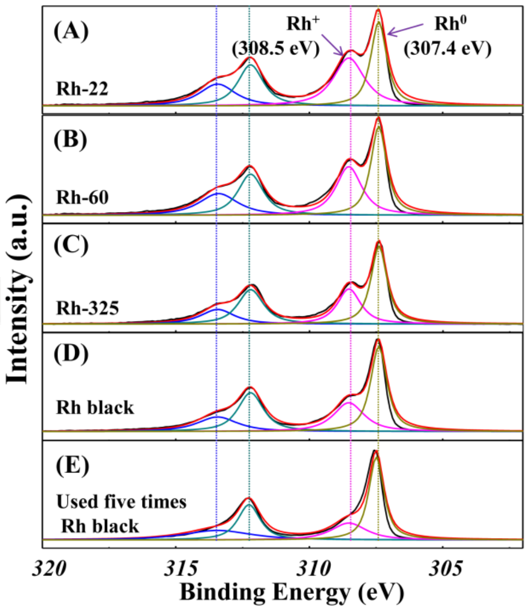


Figure 2 XPS spectra of catalysts. (A) Rh-22 mesh; (B) Rh-60 mesh; (C) Rh-325 mesh; (D) Rh black. (E) Reused five times Rh black.

Further, the electronic properties of Rh particles was determined by XPS analysis. As shown in Figure 2, The Rh $3d_{5/2}$ signals of Rh-22, Rh-60, Rh-325, Rh black and used Rh black catalysts appeared at 307.4 and 308.5 eV, which indicated the existence of Rh^+ and Rh^0 state on the surface of catalysts. However, the peak intensity of Rh^+ in used Rh black catalyst was significantly lower than other catalysts, which suggested that Rh^+ might be reduced in hydroformylation of olefins. Furthermore, the morphologies of the catalysts was characterized by SEM and TEM. SEM images of Rh-22, Rh-60, Rh-325 catalysts (Figure 3(A), 3(B), 3(C) and Figure S1(A), 1(B), 1(C)) displayed a quite rough morphology, and Rh black and used Rh black catalysts showed a morphology consisting of nanoparticles (Figure 3(D), 3(E), 3(F), and Figure S1(D)). The HR-TEM images of Rh black and used Rh black show a lattice spacing of 0.22 nm, which can be indexed to the (111) plane of Rh. The N_2 adsorption-desorption tests (Figure S2) showed that the BET surface areas of the catalysts (Table S1) were in the range of 13.4-62.4 m^2/g, and the pore radius were in the in range of 2.24-13.35 nm, Clearly, the BET surface area and pore radius of Rh balck, which is 62.4 m^2/g and 13.35 nm, respectively, are larger than other catalysts.

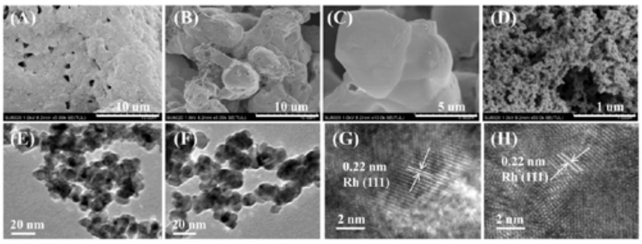


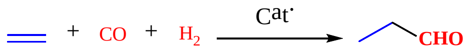
Figure 3 SEM images of (A) Rh-22 mesh; (B) Rh-60 mesh; (C) Rh-325 mesh; (D) Rh black. TEM images of (E) Rh black; (F) Rh black used five times; HR-TEM of (G) Rh black; (H) Rh black used five times.

Catalytic performance of catalysts

Then, the catalytic performance of Rh particles catalysts was tested by the hydroformylation of ethylene as model reaction (Table 1). Initial hydroformylation experiments were performed at 60 bar syngas (CO/H_2 =1:1) with toluene as solvent. Clearly, Rh black exhibited the best catalytic performance, and the desired hydroformylation product, propanal, was obtained in 64% yield (Table 1, entry 1). Lower conversions were observed in the case of other Rh particles (Rh-22, Rh-60, and Rh-325). Based on the amount of different Rh particle catalysts used, the TOFs for propanal formation of Rh-22, Rh-60, Rh-325 and Rh black are 17, 21, 33, and 200 h^{-1}, respectively (Entries 1-4). Thus, the order of catalytic performance of the different Rh particle catalysts is Rh black > Rh-325 > Rh-60 > Rh-22. It is clear that the catalytic performances of the Rh particle are strongly dependent on the size of Rh particle. In addition, the surface area and pore distribution of catalyst play important roles in catalytic activity, surface area, pore volume and average pore radius of Rh black are large than other catalysts. Therefore, Rh black is the most active catalyst. As is well known, $RhCl_3$ XH_2O, $[Rh(COD)Cl]_2$ and $Rh(CO)(acac)_2$ are classical homogeneous catalysts in hydroformylation of olefins. [66, 67] Much lower TOFs of 39 and 66 h^{-1}were obtained when $RhCl_3$ XH_2O and $[Rh(COD)Cl]_2$ were employed at the same reaction conditions (Entries 5-6).

Rh(CO)(acac)$_2$ as a catalyst showed a TOF of 161 h^{-1} (Entry 7), but it is still lower than that obtained in this work. The by-product of ethylene hydroformylation was not detected in GC-MS. The catalytic performance of Rh black has compared with supported Rh catalysts (Table S2). Surprisingly, the Rh black exhibited better catalyst activity than supported Rh catalysts except Rh-P-MMCb containing phosphine ligand.

Table 1 Screening of the catalyst for the Hydroformylation of ethylene [a].



Entry	Cat.	n/mmol[b]	Yield/ %[b]	TOF/h^{-1}
1	Rh black	3.89	64	200
2[c]	Rh-325	1.93	39	33
3[c]	Rh-60	1.24	22	21
4[c]	Rh-22	1.00	18	17
5[c]	RhCl$_3$ XH$_2$O	2.28	43	39
6	Rh(COD)Cl$_2$	1.28	24	66
7	Rh(acac)(CO)$_2$	3.13	55	161

[a] Reaction conditions: ethylene (5 mmol), [Rh] (0.01 mmol), CO (3 MPa), H$_2$ (3 MPa), 100 °C, toluene (2.0 mL), 2 h; [b] The yields of propanal were determined by GC-FID with decane as an internal standard; [c] 6 h.

Furthermore, the kinetic study on the hydroformylation of ethylene to propanal was conducted over Rh black catalyst. The evolution relationships of propanal yield with reaction time at different temperatures over Rh black catalyst were investigated (Figures 4(A), Table S3). The data points were used to construct linear -ln(1-Y) versus time plots, and the observed first-order rate constants k were obtained from the slopes of the rise lines. These results reveal that the catalytic conversion of ethylene to propanal is a pseudo first order reaction process. In addition, the apparent activation energy barrier (Ea) of the rate-determining step was calculated according to the Arrhenius equation [$k = A\ e^{(-Ea/RT)}$] based on the reaction rate constants (k) at different temperatures. An Arrhenius plot for ethylene hydroformylation in the temperature interval 87-110 °C was obtained, and the apparent activation energy for propanal formation was calculated to be 23.1 kJ•mol^{-1} (Figure 4(B)).

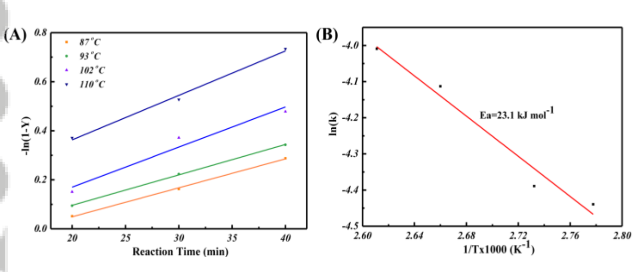
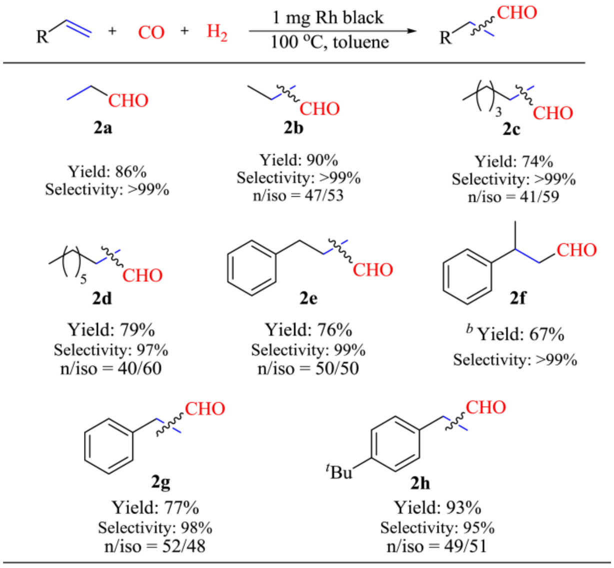


Figure 4 (A) Effect of temperature on rate of propanal synthesis. Ethylene (5 mmol), Rh black (0.01 mmol), CO (3 MPa), H$_2$ (3 MPa), toluene (2 mL); (B) Arrhenius plot for apparent activation energies of the Rh black catalyst.

Scope of the substrates

Next, we examined the substrates scope to test the efficiency of the Rh black catalyst (Table 2). Both aliphatic (ethylene, 1-propylene, 1-hexene and 1-octene) and aromatic olefins (styrene, 4-tert-butyl-styrene and α-methyl styrene) served as starting materials and afforded the desired aldehydes in good yields and chemical selectivities. As shown in Table 2, aliphatic olefins such as ethylene, 1-propylene, 1-hexene and 1-octene, were converted to the corresponding aldehydes with good yields (74-90%), excellent chemical selectivities (97-99%) and moderate regioselectivity (n/iso =40:60-47:53) (2a-2d). Similarly, the hydroformylation reaction of allylbenzene also proceeded well, affording the corresponding product in 76% yield and 99% chemical selectiviey with moderate regioselectivity (n/iso = 50:50) (2e). It should be mentioned that in the case of α-methyl styrene as the substrate, the desired linear product could be selectively obtained in 67% yield (2f). In addition, styrene and related derivatives could be also converted to the corresponding aldehydes (2g-2h) in 77-93% yields and 95-98% chemical selectivities. It was noted that substitution at the para-position of styrene had a significant electronic effect on reactivity. For examples, styrene bearing electron-donating group at the para-position led to functionalized aldehyde in 93% yield while styrene delivered benzenepropanal in 77% yield (2g vs 2h).

Table 2 Substrate scope of olefins.[a]



[a] Reaction conditions: alkenes (5 mmol), [Rh] (0.01 mmol), CO (3 MPa), H$_2$ (3 MPa), toluene (2.0 mL), 100 °C, 4 h, yields and selectivities of aldehyde were determined by GC-FID; [b] alkenes (2 mmol).

Recycling of Rh black catalyst

Finally, the recycling of Rh black catalyst in hydroformylation of ethylene was tested, as shown in Figure 5 and Table S2. For each recycling experiment, the catalyst was collected by centrifugation and sequentially washed with 50 mL ethyl acetate and dried in 80 ℃ prior to use. It was found that the Rh black catalyst can be reused at least 5 cycles with good yield of propanal. To investigate the leaching of Rh, the reaction solution after each cycle was determined by ICP-AES in Table S4, and results showed the Rh leaching is negligible after each cycle.

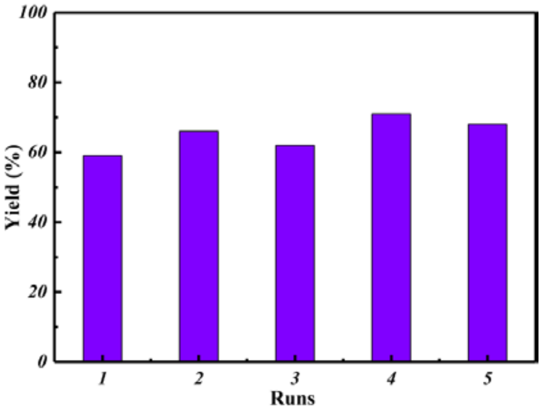


Figure 5 Stability test of catalyst: ethylene (43 mmol), Rh black (50 mg), CO (4.5 MPa), H_2 (4.5 MPa), toluene (60 mL), 100 °C, 1 h, yield was determined by GC-FID with decane as an internal standard.

Conclusions

In the present study, a simple organic ligand-free heterogeneous Rh-based catalytic system were developed for the hydroformylation of olefins. A series of functional aldehydes were synthesized by simple Rh black catalyst under optimal reaction conditions, and good yields were generally obtained. Meanwhile, this catalytic system showed good reusability, and the catalyst could be reused up to five times without loss of activity.

Experimental

All chemicals, solvent, and Rh particles were obtained commercially and used as received. The catalysts of Rh-22 mesh, Rh-60 mesh, Rh-325 mesh and Rh black were purchased from the company of Alfa Aesar, and the CAS number of Rh particles is 7440166.

Rh catalyst (0.01 mmol), olefins (5 mmol), and toluene (2 mL) were added to a stainless steel autoclave (80 mL) with a magnetic stir bar. After the autoclave was sealed and purged with CO three times, the pressure of syngas (CO/H_2=1:1) was adjusted to 6 MPa and the autoclave was put into a preheated reactor, stirring at 100 °C for 4 h. After reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with 5 mL of ethyl acetate and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt% phenyl groups and a FID detector). For recycling, the catalyst was separated by centrifugation, washed with ethyl acetate, dried at 80 °C for 12 h and used directly for the next run.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

Acknowledgement (optional)

Financial supports from the NSFC (21633013), the Cooperation Foundation of Dalian National Laboratory for Clean Energy of CAS (DNL201901), the ‘Light of West China’ Program, Fujian Innovation Academy and Key Research Program of Frontier Sciences of CAS (QYZDJ-SSW-SLH051), are gratefully acknowledged.

Data availability

The data supporting the findings of this study are available within the Article and its Supplementary Information files. All other relevant source data are available from the corresponding author upon request.

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(The following will be filled in by the editorial staff)
Manuscript received: XXXX, 2019
Manuscript revised: XXXX, 2019
Manuscript accepted: XXXX, 2019
Accepted manuscript online: XXXX, 2019
Version of record online: XXXX, 2019

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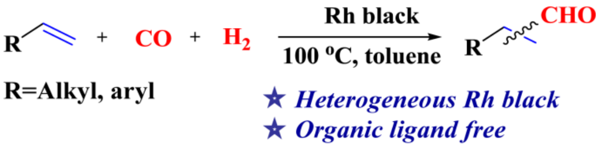

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