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ARTICLE

Designing highly efficient Rh/CPOL-bp&PPh₃ heterogenous catalysts for hydroformylation of internal and terminal olefins

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Vinyl functionalized BIPHEPHOS ligand denoted as vinyl biphephos has been successfully synthesized. Copolymerization of vinyl biphephos with tris(4-vinylphenyl) phosphane can prepare an efficient Porous Organic Polymers (POPs) CPOL-bp&PPh₃. The ultimately formed Rh/CPOL-bp&PPh₃ heterogeneous catalyst showed excellent performance in converting the terminal olefins to the corresponding linear aldehydes with high regioselectivity (I/b=96:4~98:2), activity and stability, even better than the comparable homogeneous Rh+vinyl biphephos system. Notably, isomerizing hydroformylation of internal olefins (2-heptene, 2-octene, trans-3-hexene) were also performed with high regioselectivity (I/b=92:8~93:7) using the Rh/CPOL-bp&PPh₃ heterogeneous catalyst.

Introduction

The research of novel porous organic polymers (POPs)¹ has explosively grown because of their potential applications in gas separation and storage, energy storage and conversion, light harvesting and sensing.² And various chemical reactions have been applied to fabricating POPs, including Friedel-Crafts alkylations, Yamamoto coupling, Sonogashira-Hagihara coupling, Suzuki-Miyaura, Schiff-base chemistry and boronic acid condensation.³ POPs can be mainly divided into several classes, such as hypercrosslinked polymers (HCPs),⁴ polymers of intrinsic microporosity (PIMs)⁵ and covalent organic frameworks (COFs).⁶ Among of them, HCPs and PIMs are amorphous, while COFs is crystalline.

Recently, Xiao⁷ developed novel template-free and metal-free routes for synthesis of hierarchically porous organic polymers. The nanoporous polydivinylbenzene materials with high surface area, large pore volume, controllable average pore size, superhydrophobicity and superoleophilicity were successfully synthesized by a novel solvothermal route. Compared with other routes to construct POPs, the solvothermal route are more environmentally friendly and economically beneficial. The porous organic polymers formed by this novel irreversible polymerization may disclose new perspectives for the design of heterogeneous catalysts.

It is well known that hydroformylation is one of the most important examples of homogeneously catalysed reactions in industry for the synthesis of aldehydes (more than 10 million tons every year).⁸ The aldehydes are versatile intermediates and building blocks for various pharmaceuticals, agrochemicals, commodities and fine chemicals.⁹ Both branched and linear aldehydes can be formed, but linear aldehydes are the more desired products due to their more prevalent use in downstream processes. Particularly, the long-chain aldehydes from hydroformylation of long-chain olefins were widely used to produce surfactants, detergents and plasticizers, and it is of high interest to apply the highly active, stable and linear selective catalysed systems for hydroformylation of long-chain olefins.¹⁰

Previously, we reported a universal route for synthesizing a new class of POPs, porous organic ligands (POLs) with high surface area, large pore volume and hierarchical porosity.¹¹ Notably, Rh/POL-PPh₃ heterogeneous catalysts showed excellent activity and stability in hydroformylation of 1-octene. However, the linear selectivity of this system remains modest. To achieve a highly linear selectivity, numerous ligands including Bisbi, Xantphos, Biphephos and Naphos with high steric hindrance and suitable bite angle emerged in the last decades, and were used in the homogeneously catalyzed hydroformylation reactions with high regioselectivity.¹² Among them, Biphephos is weak σ-donor but strong π-acceptor, which can facilitate the CO dissociation from the metal centers in the catalytic species, this lead to the high activity of Rh-Biphephos system. Besides, P-Rh-P angle of 120° in Rh-BIPHEPHOS complex lead to superior linear-regioselectivity.¹³ In order to heterogenizing Rh-BIPHEPHOS system, Tunge¹⁴ developed a recyclable catalytic system using JanaPhos

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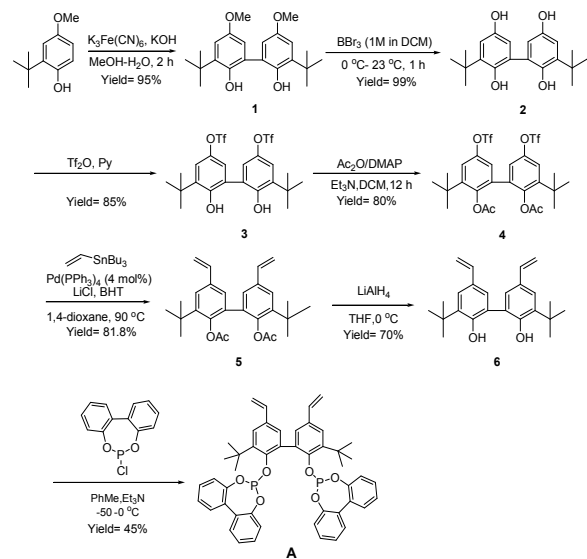
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**Scheme 1.** Synthesis of vinyl biphenphos

Catalyst, in which 2,2'-bisphenoxy-phosphorus chloride was linked to the polymer with quite low degree of polymerization in order to make the catalyst soluble in nonpolar solvents but insoluble in polar solvents. However, the ratio of linear to branched aldehyde in the products of 1-octene hydroformylation was only 3.35. More recently, Xiao¹⁵ immobilized a series of diphosphine ligand by polymerization. But these polymers self-supported Rh catalysts showed poor linear selectivity (l/b ratio was only 2.63 in the products of 1-octene hydroformylation), due to the poor steric hindrance of the corresponding diphosphine ligands.

In this communication, we report a strategy to prepare porous organic copolymers self-supported Rh heterogeneous catalyst with high regioselectivity and stability for hydroformylation of terminal and internal olefins. Our key methodology of strategy is copolymerization of sterically hindered bidentate and monodentate ligands to obtain the highly regioselective and stable heterogeneous catalysts. A vinyl-functionalized BIPHEPHOS denoted as vinyl biphenphos has been successfully synthesized in our laboratories according to the routes listed in Scheme 1, and was copolymerized with tris(4-vinylphenyl)phosphane to prepare efficient porous organic copolymers as both ligand and support for hydroformylation.

Experimental

Materials

All solvents were purified according to standard laboratory methods. THF was distilled over sodium/benzophenone under N₂ atmosphere. Toluene and acetonitrile were distilled over calcium hydride under N₂ atmosphere for deoxygenation and dehydration. Azobisisobutyronitrile (AIBN) and PCl₃ were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. PCl₃

was purified by distillation under nitrogen atmosphere before use. Rh(CO)₂(acac) (99%), 1-hexene (97%), 1-octene (99%) and 1-heptene (98%) were obtained from J&K Scientific Ltd. 2-octene (cis- and trans- mixture, >98.0%), 2-heptene (cis- and trans- mixture, >98.0%) and trans-3-hexene (>99.0%) were obtained from TCI (Shanghai) Development Co., Ltd. Tris(4-vinylphenyl) phosphane (denoted as 3vPPh₃ for short) was synthesized according to the literature.^{11a}

Methods

Unless otherwise noted, all manipulations were carried out under N₂ atmosphere either in a glove-box or using standard Schlenk techniques.

Synthesis of vinyl biphenphos

Interesting and challenging vinyl biphenphos was synthesized in our laboratories according to the routes listed in Scheme 1. The successful synthesis of vinyl biphenphos was further confirmed by HRMS (High Resolution Mass Spectrum). And the NMR characterization of intermediates 1-7 in vinyl biphenphos synthesis are listed in details in Supporting Figures.

Synthesis of CPOL-bp&PPh₃

CPOL-bp&PPh₃ was synthesized from copolymerization of vinyl biphenphos and tris(4-vinylphenyl) phosphane under solvothermal condition in an autoclave. As a typical run, 1.0 g of tris(4-vinylphenyl)phosphane and 0.25 g of vinyl biphenphos was dissolved in 10 mL of THF under N₂ atmosphere, followed by the addition of 25 mg of AIBN. After stirring for 10 minutes, the mixture was then transferred into an autoclave to occur polymerization reaction at 100 °C for 24 h. After evaporation of THF at 65 °C under vacuum, a solid monolith named as CPOL-bp&PPh₃ was obtained.

Synthesis of Rh/CPOL-bp&PPh₃ heterogeneous catalyst

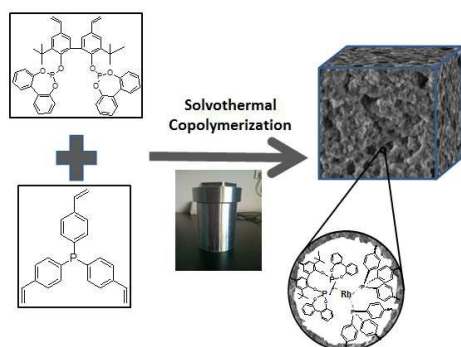
As a typical run, 3.7 mg of Rh(CO)₂(acac) was dissolved in 20 mL of THF under N₂ atmosphere, followed by the addition of 1.0 g of CPOL-bp&PPh₃. After stirring for 24 h under N₂ atmosphere at room temperature and evaporation of THF at 65 °C under vacuum, Rh/CPOL-bp&PPh₃ catalyst was finally obtained. The metal loading was determined by inductively coupled plasma (ICP) analysis.

Characterizations of the catalyst

Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Quantachrome Autosorb-1 system. The samples were outgassed for 10 h at 393 K before the measurements. The specific 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.

The thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449F3), the samples were heated at the rate of 10 K/min from room temperature up to 923 K under a nitrogen atmosphere.

Transmission electron microscope (TEM) images were performed using a JEM-2100 with accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was performed using a JSM-7800F.



Scheme 2. Synthesis of Rh/CPOL-bp&PPh₃ catalysts.

Table 1. Textural parameters of CPOL-bp&PPh₃ and Rh/CPOL-bp&PPh₃.

Samples	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)
CPOL-bp&PPh ₃	1088.0	2.07
Rh/CPOL-bp&PPh ₃	985.3	1.94

Inductively coupled plasma (ICP) was measured on an ICPS-8100 apparatus.

Solid-state ³¹P MAS NMR experiments were recorded on a VARIAN Infinity plus spectrometer equipped with a 2.5 mm probe at a frequency of 161.8 MHz. The experiments were recorded under a magic angle spinning rate of 10 kHz and a delay of 3.0 s. Solid-state ³¹P NMR chemical shifts were referenced to 85% H₃PO₄. And ¹³C MAS NMR spectra were recorded under a magic angle spinning rate of 6 kHz.

Powder X-ray diffraction (XRD) data were collected on PANalytical EMPYREAN using Cu K α radiation.

The XPS was conducted using a Thermo Scientific and the spectrometer binding energy was calibrated through the reference C 1s (284.6 eV).

Catalyst tests

All the hydroformylation experiments were performed in a stainless steel autoclave (30 mL) equipped with a magnetic bar. For a typical run, 5 mL of toluene, 1 g of 1-octene, and 0.1224 g of Rh/CPOL-bp&PPh₃ catalyst were added into the autoclave. After sealing and purging with syngas (CO/H₂=1:1) for 6 times, the autoclave was heated to 100 °C within 30 min, followed by adjusting the pressure of syngas to 1.0 MPa and stirring at 100 °C for 4 h. During the reaction, the pressure in the reactor was held by injection of syngas (CO/H₂=1:1) via a pressure regulator. After cooling the autoclave in an ice bath and releasing the pressure, the sample was taken from autoclave by filtration or centrifugation and analyzed by gas chromatography (Agilent 7890A gas chromatography with an HP-5 column, using an FID detector and n-butanol as an

internal standard). After 2 times washing with degassed toluene, the catalyst can be directly used in the next run.

Results and discussion

Characterizations of the Rh/CPOL-bp&PPh₃ catalyst

CPOL-bp&PPh₃ carrier was characterized by solid NMR, thermogravimetry (TG), nitrogen adsorption-desorption analysis and X-ray diffraction (XRD). ¹³C MAS NMR spectrum (Fig. 1A) exhibits a quite small peak at 113 ppm corresponding to vinyl groups, indicating the high degree of polymerization of CPOL-bp&PPh₃ carrier (Fig. S1, ESI). In the ³¹P MAS NMR spectrum (Fig. 1B) of fresh CPOL-bp&PPh₃, two peaks at 146.3 ppm and -5.6 ppm are in agreement with the corresponding monomers vinyl biphenyl phosphine and tris(4-vinylphenyl)phosphane. ³¹P MAS NMR spectrum also exhibits an additional small peak at 23.9 ppm corresponding to an oxidation state of phosphorus (P=O), which indicates slight oxidation of P atoms during the polymerization (see ESI, Figure S2). Remarkably, the ³¹P MAS NMR spectrum of Rh/CPOL-bp&PPh₃ shows the peak at 23.7 ppm with a relatively large peak area, which can be assigned to both oxidation state of phosphorus (P=O) and those PPh₃ coordinated with Rh as well. Besides, compared with CPOL-bp&PPh₃, 0.140% wt Rh/CPOL-bp&PPh₃ gives relatively low-field peak at 144.8 ppm. The low-field shift can be ascribed to the biphenyl units coordinated with Rh. In figure S3, XPS of Rh(CO)₂(acac) shows the binding energies of Rh3d_{3/2} and Rh3d_{5/2} at 314.0 eV and 309.2 eV respectively. In 0.14% Rh/CPOL-bp&PPh₃ catalyst, the binding energies of Rh3d_{3/2} and Rh3d_{5/2} decrease to 313.4 eV and 308.6 eV, showing the successful coordination of Rh(CO)₂acac with CPOL-bp&PPh₃ carrier. Interestingly, compared with XPS spectra of P2p in CPOL-bp&PPh₃ (two kinds of P species: PPh₃ units at 131.8 eV, biphenyl units at 132.9 eV), 0.14% Rh/CPOL-bp&PPh₃ give relatively higher binding energy (131.9 eV, 133.0 eV), indicating the successful coordination of Rh with

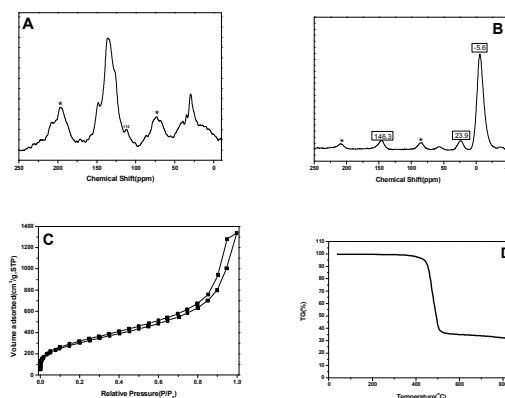


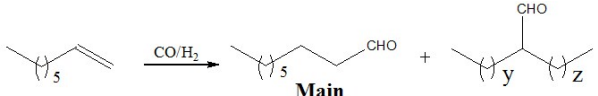
Figure 1. (A) ¹³C MAS NMR spectrum, (B) ³¹P MAS NMR spectrum, (C) N₂ sorption isotherms, (D) TG curve, (E) TEM image, and (F) SEM image of CPOL-bp&PPh₃.

two kinds of P species in the polymer skeleton. Nitrogen sorption isotherm (Fig. 1C) exhibits the curve of type-I plus type-IV, indicating the CPOL-bp&PPh₃ carrier possesses hierarchical porosity, which is further confirmed by TEM images and SEM images (Fig. S6-9, ESI). The pore sizes are distributed at 0.70, 0.84, 1.38, 2-18 nm according to the pore size distribution curve calculated from non-local density functional theory (NLDFT) (Figure S5). Table 1 shows the high BET surface area and large pore volume of CPOL-bp&PPh₃, which is desirable for the dispersion of active sites. In the corresponding Rh/CPOL-bp&PPh₃ catalyst, BET surface area and total pore volume are still as high as 985.3 m² g⁻¹ and 1.94 cm³ g⁻¹, without any significant differences compared to CPOL-bp&PPh₃ carrier. TG shows that CPOL-bp&PPh₃ giving the starting decomposition temperature higher than 430 °C, demonstrating the superior thermal stability (Fig. 1D). XRD indicates CPOL-bp&PPh₃ as amorphous porous organic polymers (POPs) (Fig. S10, ESI).

Catalyst performance tests on hydroformylation

The hydroformylation of 1-octene was selected to evaluate the performance of Rh/CPOL-bp&PPh₃ catalyst under different temperature and pressure of syngas. We employed excess substrates (S/C=20000) to make sure the reliability of the obtained data. As shown in table 2, the high pressure of syngas (CO:H₂=1:1) suppressed the formation of alkane and iso-alkenes. Besides, the high pressure also promoted the selectivity of aldehydes. But under higher pressure, the linear selectivity and activity were also damaged. Thus we chose the milder pressure of 1MPa to maintain the selectivity of aldehydes as well as suppress the formation of alkane and iso-alkenes. Temperature also plays significant role on the performance of Rh/CPOL-bp&PPh₃ catalyst. Under 60 and 80 °C, the selectivity of aldehydes and l/b ratio was high, but the conversion of 1-octene remained modest (Table 3). Under higher temperature

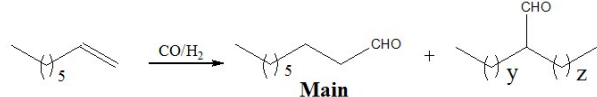
Table 2. The influence of pressure of syngas on hydroformylation of 1-octene over Rh/CPOL-bp&PPh₃ catalyst^a



Pressure/ MPa	Conv./ %	Aldehydes/ %	Iso- alkenes/ %	Alkane/ %	l/b ratio
0.5	94.4	13.8	75.8	10.4	97:3
1	93.1	19.9	72.2	7.9	97:3
2	92.9	18.0	74.7	7.3	97:3
3	89.0	27.5	66.7	5.7	97:3
4	77.0	28.0	66.9	5.1	95:5

^aReaction conditions: 0.0612g Rh/CPOL-bp&PPh₃ catalyst (Rh loading at 0.14 wt%), S/C=20000, toluene (5.0 g), 100 °C for 1 h. Syngas: CO:H₂=1:1.

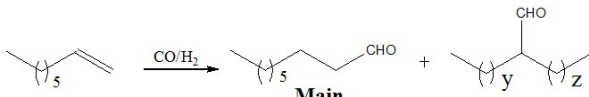
Table 3. The influence of temperature on hydroformylation of 1-octene over Rh/CPOL-bp&PPh₃ catalyst^a



Temperature/ °C	Conv./ %	Aldehydes/ %	Iso- alkenes/ %	Alkane/ %	l/b ratio
60	20.7	57.6	38.1	4.3	97:3
80	66.9	58.0	37.8	4.1	98:2
100	93.1	19.9	72.2	7.9	97:3
130	96.0	11.7	55.1	33.2	86:14
160	95.9	10.9	48.1	41.0	80:20

^a Reaction conditions: 0.0612g Rh/CPOL-bp&PPh₃ catalyst (Rh loading at 0.14 wt%), S/C=20000, toluene (5.0 g), 1.0 MPa for 1 h. Syngas: CO:H₂=1:1.

Table 4. Hydroformylation of 1-octene using different catalysts^a



Entry	Catalysts	Conv. (%)	Select. (%) ^b	l:b ratio
1	Rh(CO) ₂ (acac) ^c	98.5	13.6	35:65
2	Rh(CO) ₂ (acac)+vinyl biphephos ^d	97.4	40.3	94:6
3	Rh(CO) ₂ (acac)+Biphephos ^e	96.8	31.2	94:6
4	Rh(CO) ₂ (acac)+3vPPh ₃ ^f	96.6	89.0	77:23
5	Rh/POL-PPh ₃ ^g	98.3	73.9	53:47
6	Rh/CPOL-bp&PPh ₃ ^h	97.1	58.4	98:2

^a Reaction conditions: 0.1224 g catalyst (Rh loading at 0.14 wt%), CO/H₂=1:1 (1.0 MPa), S/C=5400, toluene(5.0 g), 100 °C for 4 h.

^b Total selectivity of aldehydes and other products are iso-olefins, which can be converted to starting olefins again along with the consumption of feed-stocks.

^c 0.17 mg of Rh(CO)₂(acac), S/C=5400.

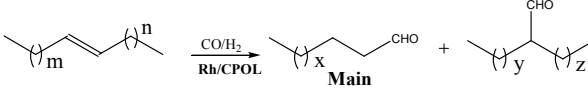
^d 0.17 mg of Rh(CO)₂(acac)+24.48 mg of vinyl biphephos. Rh:vinyl biphephos=1:18.9. S/C=5400.

^e 0.17 mg of Rh(CO)₂(acac)+24.75 mg of Biphephos. Rh:Biphephos=1:18.9. S/C=5400.

^f 0.17 mg of Rh(CO)₂(acac)+97.92 mg of 3vPPh₃. Rh:3vPPh₃=1:172.9. S/C=5400.

^g 0.1224 g catalyst (Rh loading at 0.14 wt%). S/C=5400.


^h 0.1224 g catalyst (Rh loading at 0.14 wt%). S/C=5400. Rh:bp:PPh₃=1:18.9:172.9. S/C=5400.

Table 5. Long-chain olefins Hydroformylation on Rh/CPOL-bp&PPh₃ catalyst^a


Entry	Olefin	Conv. (%)	Select. (%) ^b	l:b ratio
1	1-hexene	98.7	32.7	96:4
2	1-heptene	98.6	51.7	98:2
3	1-octene	97.1	58.4	98:2
4	2-heptene	34.7	41.1	92:8
5	2-octene	70.3	54.7	93:7
6	Trans-3-hexene	56.2	42.4	93:7

^a Reaction conditions: 0.1224 g catalyst (Rh loading at 0.14 wt%), CO/H₂=1:1 (1.0 MPa), S/C=5400, toluene(5.0 g), 100 °C for 4 h.

^b Total selectivity of aldehydes and other products are iso-olefins, which can be converted to starting olefins again along with the consumption of feed-stocks.

Table 6. Recycling studies of hydroformylation of 1-octene over Rh/CPOL-bp&PPh₃ catalyst^a


Run	Conv./%	Aldehydes/%	Iso-alkenes/%	Alkane/%	l/bratio
1	97.1	58.4	28.7	12.9	98:2
2	97.5	59.3	30.8	9.9	97:3
3	97.4	60.1	31.2	8.8	94:6
4	97.4	61.5	30.9	7.6	96:4
5	97.4	64.4	29.3	6.4	94:6
6	97.7	59.2	32.4	8.4	96:4

^a Reaction conditions: 0.1224 g catalyst (Rh loading at 0.14 wt%), CO/H₂=1:1 (1.0 MPa), S/C=5400, toluene(5.0 g), 100 °C for 4 h.

(130 and 160 °C), the selectivity and l/b ratio decreased significantly although the conversion of 1-octene was very high. Under 100 °C, the conversion of 1-octene was high, and the selectivity of aldehydes and l/b ratio were also acceptable. To compare the performances of different catalysis system, we also chose the model reaction of 1-octene (Table 4). The reaction temperature and pressure were fixed at 100 °C and 1 MPa. Without the ligands, Rh(CO)₂(acac) showed good conversion of 1-octene, but the selectivity of aldehydes and l/b ratio was very low. The Rh(CO)₂(acac)+vinyl biphephos system showed the conversion of 97.4%, the selectivity of 40.3%, the l/b ratio of 94:6. The Rh(CO)₂(acac)+Biphephos system showed a similar conversion and l/b ratio with the Rh(CO)₂(acac)+vinyl biphephos system, but the selectivity of aldehydes was lower. Using Rh(CO)₂(acac)+3vPPh₃ system, the conversion of 1-

octene and the selectivity of aldehydes were very exciting, but the l/b ratio was only 77:23. Our previously Rh/POL-PPh₃ catalyst showed satisfactory conversion and selectivity of aldehydes, but the linear selectivity of aldehydes was also very poor (l/b=53:47). The l/b ratio of aldehydes was up to 98:2 using Rh/CPOL-bp&PPh₃ catalyst while the conversion and selectivity of aldehydes also maintained at high level. We can come to the conclusion that Rh/CPOL-bp&PPh₃ catalyst has combined the advantages of Rh+vinyl biphephos and Rh+3vPPh₃ system.

Next, we examined the scope of substrates to test the efficiency of Rh/CPOL-bp&PPh₃ catalyst. Both terminal olefins (1-hexene, 1-heptene, and 1-octene) and internal olefins (2-heptene, 2-octene and trans-3-hexene) were served as the starting materials. As shown in table 5, the Rh/CPOL-bp&PPh₃ catalyst was very helpful for the hydroformylation of different terminal and internal olefins. The main by-products are the correspondingly isomerized olefins, which could be converted to starting olefins again along with the consumption of feed-stocks because of the equilibrium of the isomerized olefins and starting olefins. Terminal olefins, 1-hexene, 1-heptene and 1-octene, were converted to the corresponding linear aldehydes with good activity and regioselectivity. The ratios of linear to branched aldehydes were as high as 96:4-98:2, while the conversion were more than 97%. Notably, the biggest advantage of Rh/CPOL-bp&PPh₃ catalyst was to convert the internal olefins to the corresponding linear aldehydes. Tandem isomerizing hydroformylation of the internal olefins, 2-heptene, 2-octene and trans-3-hexene, to linear aldehydes can also be conducted effectively on the catalyst with ratio of l/b as high as 92:8-93:7. The catalyst can be easily recovered by simple filtration or centrifugation procedure.

Besides, 1-octene was chosen to test the stability of the catalyst, it was shown that Rh/CPOL-bp&PPh₃ catalyst can be reused at least 6 cycles with high activity and selectivity (Table 6). The Rh leaching of Rh/CPOL-bp&PPh₃ catalyst is negligible after 6 runs according to ICP investigations (Table S1, ESI), which may be ascribed to the strong multi-coordination bonds between Rh species and the exposed P species of high concentration in the catalyst.^{16, 11b}

Conclusions

To conclude, vinyl biphephos has been successfully synthesized, based on which we have developed efficient Rh/CPOL-bp&PPh₃ heterogeneous catalyst. The catalyst showed good performance in converting terminal olefins to corresponding aldehydes with high regioselectivity (l/b=96:4~98:2), activity and stability. And Isomerizing hydroformylation of internal olefins were also conducted with high regioselectivity (l/b=92:8~93:7) using this heterogeneous catalyst. Besides, it was shown that Rh/CPOL-bp&PPh₃ heterogeneous catalyst exhibited even better performance than the comparable homogeneous Rh+vinyl biphephos system. We envision that this copolymerization strategy may be one of the most promising platforms for the deployment of highly efficient heterogeneous catalysts.

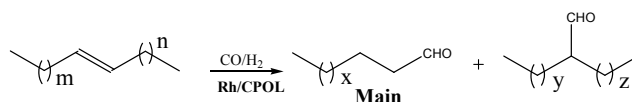
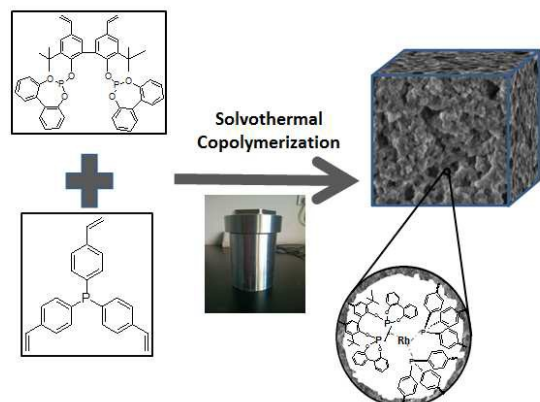
Acknowledgements

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References

- 1 a) Y. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, 2012, **41**, 2083; b) S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548; c) Q. Sun, Z. Dai, X. Meng, L. Wang and F.-S. Xiao, *ACS Catal.*, 2015, **5**, 4556; d) Q. Sun, Z. Dai, X. Meng and F.-S. Xiao, *Chem. Soc. Rev.*, 2015, **44**, 6018.
- 2 X. Zhuang, F. Zhang, D. Wu and X. Feng, *Adv. Mater.*, 2014, **26**, 3081.
- 3 Y. Jin, Y. Zhu and W. Zhang, *CrystEngComm.*, 2013, **15**, 1484.
- 4 a) Y. Luo, B. Li, W. Wang, K. Wu and B. Tan, *Adv. Mater.*, 2012, **24**, 5703; b) C. D. Wood, B. Tan, A. Trewin, H. Niu, D. Bradshaw, M. J. Rosseinsky, Y. Z. Khimyak, N. L. Campbell, R. Kirk, E. Stöckel and A. I. Cooper, *Chem. Mater.*, 2007, **19**, 2034.
- 5 a) J. Weber and A. Thomas, *J. Am. Chem. Soc.*, 2008, **130**, 6334; b) N. B. McKeown, B. Gahnem, K. J. Msayib, P. M. Budd, C. E. Tattershall, K. Mahmood, S. Tan, D. Book, H. W. Langmi and A. Walton, *Angew. Chem. Int. Ed.*, 2006, **45**, 1804.
- 6 a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166; b) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science*, 2007, **316**, 268; c) F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki and O. M. Yaghi, *J. Am. Chem. Soc.*, 2011, **133**, 11478; d) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 4570.
- 7 Y. Zhang, S. Wei, F. Liu, Y. Dua, S. Liu, Y. Ji, T. Yokoi, T. Tatsumi and F.-S. Xiao, *Nano Today*, 2009, **4**, 135.
- 8 a) R. Franke, D. Selent and A. Börner, *Chem. Rev.*, 2012, **112**, 5675; b) H. Nowothnick, A. Rost, T. Hamerla, R. Schomäcker, C. Müller and D. Vogt, *Catal. Sci. Technol.*, 2013, **3**, 600; c) X. Fang, M. Zhang, R. Jackstell and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 4645; d) S. Aguado-Ullate, J. A. Baker, V. González-González, C. Müller, J. D. Hirst and J. J. Carbó, *Catal. Sci. Technol.*, 2014, **4**, 979; e) J. Pospesch, I. Fleischer, R. Franke, S. Buchholz and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 2852; f) C. Kubis, W. Baumann, E. Barsch, D. Selent, M. Sawall, R. Ludwig, K. Neymeyr, D. Hess, R. Franke and A. Börner, *ACS Catal.*, 2014, **4**, 2097; g) M. C. de Freitas, K. C. B. de Oliveira, A. de Camargo Faria, E. N. dos Santos and E. V. Gusevskaya, *Catal. Sci. Technol.*, 2014, **4**, 1954.
- 9 a) S. Güven, B. Hamers, R. Franke, M. Priske, M. Becker and D. Vogt, *Catal. Sci. Technol.*, 2014, **4**, 524; b) S. Yu, X. Zhang, Y. Yan, C. Cai, L. Dai and X. Zhang, *Chem. Eur. J.*, 2010, **16**, 4938; c) X. Jia, Z. Wang, C. Xia and K. Ding, *Catal. Sci. Technol.*, 2013, **3**, 1901; d) G. M. Torres, R. Frauenlob, R. Franke and A. Börner, *Catal. Sci. Technol.*, 2015, **5**, 34; e) G. Liu, K. Huang, C. Cai, B. Cao, M. Chang, W. Wu and X. Zhang, *Chem. Eur. J.*, 2011, **17**, 14559.
- 10 a) O. Diebolt, C. Müller and D. Vogt, *Catal. Sci. Technol.*, 2012, **2**, 773; b) K. Takahashi, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2012, **134**, 18746; c) L. Obrecht, P. C. J. Kamer and W. Laan, *Catal. Sci. Technol.*, 2013, **3**, 541; d) U. Gellrich, T. Koslowski and B. Breit, *Catal. Sci. Technol.*, 2015, **5**, 129; e) H. Klein, R. Jackstell, K.-D. Wiese, C. Borgmann and M. Beller, *Angew. Chem. Int. Ed.*, 2001, **40**, 3408.
- 11 a) Q. Sun, M. Jiang, Z. Shen, Y. Jin, S. Pan, L. Wang, X. Meng, W. Chen, Y. Ding, J. Li and F.-S. Xiao, *Chem. Commun.*, 2014, **50**, 11844; b) M. Jiang, L. Yan, Y. Ding, Q. Sun, J. Liu, H. Zhu, R. Lin, F. Xiao, Z. Jiang, J. Liu, *J. Mol. Catal. A: Chem.*, 2015, **404-405**, 211.
- 12 a) X. Jia, Z. Wang, C. Xia and K. Ding, *Chem. Eur. J.*, 2012, **18**, 15288; b) K. Dong, X. Fang, R. Jackstell and M. Beller, *Chem. Commun.*, 2015, **51**, 5059; c) S. Li, K. Huang, J. Zhang, W. Wu and X. Zhang, *Org. Lett.*, 2013, **15**, 3078; d) S. Yu, Y. Chie, Z. Guan, Y. Zou, W. Li and X. Zhang, *Org. Lett.*, 2009, **11**, 241; e) P. Dydio, W. I. Dzik, M. Lutz, B. de Bruin and J. N. H. Reek, *Angew. Chem. Int. Ed.*, 2011, **50**, 396; f) S. Yu, Y. Chie, Z. Guan and X. Zhang, *Org. Lett.*, 2008, **10**, 3469; g) C. Cai, S. Yu, B. Cao and X. Zhang, *Chem. Eur. J.*, 2012, **18**, 9992.
- 13 a) G. D. Cuny and S. L. Buchwald, *J. Am. Chem. Soc.*, 1993, **115**, 2066; b) B. Moasser and W. L. Gladfelter, *Organometallics*, 1995, **14**, 3832; c) A. Behr, D. Obst and B. Turkowski, *J. Mol. Catal. A: Chem.*, 2005, **226**, 215; d) G. Kiedorf, D. M. Hoang, A. Müller, A. Jörke, J. Markert, H. Arellano-Garcia, A. Seidel-Morgenstern, C. Hamel, *Chem. Eng. Sci.*, 2014, **115**, 31; e) A. Behr, D. Obst, C. Schulte, T. Schosser, *J. Mol. Catal. A: Chem.*, 2003, **206**, 179; f) C. Vogl, E. Paetzold, C. Fischer, U. Kragl, *J. Mol. Catal. A: Chem.*, 2005, **232**, 41.
- 14 a) R. Jana and J. A. Tunge, *J. Org. Chem.*, 2011, **76**, 8376; b) R. Jana and J. A. Tunge, *Org. Lett.*, 2009, **11**, 971.
- 15 Q. Sun, Z. Dai, X. Liu, N. Sheng, Feng Deng, X. Meng and F.-S. Xiao, *J. Am. Chem. Soc.*, 2015, **137**, 5204–5209.
- 16 a) H. Zhang, X. Pan, X. Han, X. Liu, X. Wang, W. Shen and X. Bao, *Chem. Sci.*, 2013, **4**, 1075; b) F. Liu, L. Wang, Q. Sun, L. Zhu, X. Meng and F.-S. Xiao, *J. Am. Chem. Soc.*, 2012, **134**, 16948; c) Z. Chen, Z. Guan, M. Li, Q. Yang and C. Li, *Angew. Chem. Int. Ed.*, 2011, **50**, 4913.

Designing highly efficient Rh/CPOL-bp&PPh₃ heterogenous catalysts for hydroformylation of internal and terminal olefins



Entry	Olefin	Conv. (%)	Select. (%)	l:b ratio
1	1-hexene	98.7	32.7	96:4
2	1-heptene	98.6	51.7	98:2
3	1-octene	97.1	58.4	98:2
4	2-heptene	34.7	41.1	92:8
5	2-octene	70.3	54.7	93:7
6	Trans-3-hexene	56.2	42.4	93:7

High regioselectivity! Good recyclability!