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

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1. Supporting Figures

Figure S1. (A) $^{13}$C MAS NMR spectrum of CPOL-bp&PPh$_3$, (B) $^{13}$C NMR spectrum of tris(4-vinphenyl)phosphane and (C) $^{13}$C NMR spectrum of vinyl biphephos.

The peaks at 113 ppm in CPOL-bp&PPh$_3$, which can be assigned to unpolymerized vinyl groups, are quite small compared with the corresponding monomers (B, C), indicating that CPOL-bp&PPh$_3$ has high degree of polymerization. The peaks at * are side bands.
Figure S2. $^{31}$P MAS NMR spectra of (A) CPOL-bp&PPh$_3$, (B) 0.14 % wt Rh/CPOL-bp&PPh$_3$ and (C) 2.0 % wt Rh/CPOL-bp&PPh$_3$. $^{31}$P NMR spectra of (D) tris(4-vinphenyl)phosphane and (E) vinyl biphephos. The peaks at * are side bands. The $^{31}$P MAS NMR spectrum of fresh CPOL-bp&PPh$_3$ exhibits an additional small peak at 23.9 ppm corresponding to an oxidation state of phosphorus (P=O), which indicates that slight oxidation of P atom took place during the polymerization. Remarkably, the $^{31}$P MAS NMR spectrum of fresh 0.14 % wt Rh/CPOL-bp&PPh$_3$ shows that the peak at 23.7 ppm could be assigned to both oxidation state of phosphorus (P=O) and those PPh$_3$ coordinated with Rh as well. 2.0 % wt Rh/CPOL-bp&PPh$_3$ shows higher peak at 24.0 ppm than 0.14 % wt Rh/CPOL-bp&PPh$_3$, indicating more PPh$_3$ units are coordinated with Rh. Besides, compared with the peak at 146.3 ppm in CPOL-bp&PPh$_3$, 0.14% wt Rh/CPOL-bp&PPh$_3$ gives relatively low-field peak at 144.8 ppm, 2.0 % wt Rh/CPOL-bp&PPh$_3$ gives relatively low-field peak at 144.6 ppm. The low-field shift can be ascribed to the biphephos units coordinated with Rh.
Figure S3. (A) Rh3d XPS spectra of Rh(CO)$_2$(acac), (B) Rh3d XPS spectra of 0.14% Rh/CPOL-bp&PPH$_3$, (C) P2p XPS spectra of CPOL-bp&PPH$_3$, (E) P2p XPS spectra of 0.14% Rh/CPOL-bp&PPH$_3$.

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&PPH$_3$ 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)$_2$(acac) with CPOL-bp&PPH$_3$ carrier. Interestingly, compared with XPS spectra of P2p in CPOL-bp&PPH$_3$ (two kinds of P species: PPH$_3$ units at 131.8 eV, biphphos units at 132.9 eV), 0.14% Rh/CPOL-bp&PPH$_3$ give relatively higher binding energy (131.9 eV, 133.0 eV), indicating the successful coordination of Rh with two kinds of P species in the polymer skeleton.
Figure S4. Nitrogen sorption isotherms of (A) CPOL-bp&PPh$_3$ and (B) Rh/CPOL-bp&PPh$_3$.

Figure S4 indicates that N$_2$ sorption isotherm of both CPOL-bp&PPh$_3$ and Rh/CPOL-bp&PPh$_3$ give the curve of type-I plus type-IV, showing that the two samples possess both micropores and mesoporous.
Figure S5. Pore size distribution of (A) CPOL-bp&PPh$_3$ and (B) Rh/CPOL-bp&PPh$_3$.

Pore size distribution is calculated from non-local density functional theory (NLDFT). Figure S5 indicates that both CPOL-bp&PPh$_3$ and Rh/CPOL-bp&PPh$_3$ possess hierarchical porosity.
Figure S6. TEM images of CPOL-bp&PPh₃.
Figure S7. TEM images of Rh/CPOL-bp&PPh₃.
Figure S8. TEM images of Rh/CPOL-bp&PPh$_3$ after 6 runs.
Figure S9. SEM images of (A) CPOL-bp&PPh₃, (B) Rh/CPOL-bp&PPh₃ and (C) Rh/CPOL-bp&PPh₃ after 6 runs.

Figure S9 shows that all the samples have hierarchical porosity.
Figure S10. XRD of (A) CPOL-bp&PPh₃, (B) Rh/CPOL-bp&PPh₃ and (C) Rh/CPOL-bp&PPh₃ after 6 runs.

XRD also show that all three samples are amorphous.
2. Supporting Tables

Table S1. Rh concentration of fresh and spend catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rh content (wt.%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/CPOL-bp&amp;PPh&lt;sub&gt;3&lt;/sub&gt; (fresh sample)</td>
<td>0.1385%</td>
</tr>
<tr>
<td>Rh/CPOL-bp&amp;PPh&lt;sub&gt;3&lt;/sub&gt; (spend sample, 6 runs)</td>
<td>0.1340%</td>
</tr>
</tbody>
</table>

<sup>a</sup> The lowest detectable limit of ICP-OES is 10<sup>-6</sup>, “85” and “40” in Rh content are untrusted data.
3. NMR characterizations of compounds in Scheme 1

Analytical data for compounds 1-7 and A, B

$^1$H and $^{13}$C spectra were recorded on a 500 MHz spectrometer. Chemical shifts were reported in ppm. $^1$H NMR spectra were referenced to TMS in CDCl$_3$ (0 ppm) or d$_6$-DMSO (0 ppm), and $^{13}$C-NMR spectra were referenced to CDCl$_3$ (77.0 ppm) or d$_6$-DMSO (39.5 ppm). All $^{13}$C-NMR spectra were measured with complete proton decoupling except compound (A). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz.

Mass spectroscopy were recorded on a Esquire 3000 Plus mass spectrometer. We were grateful to the assistance of the Department of Chemistry, Xiamen University in obtaining the MS data.

5,5'-dimethoxy-3,3'-di-tert-butylbiphenyl-2,2'-diol (1)

![Structure of 5,5'-dimethoxy-3,3'-di-tert-butylbiphenyl-2,2'-diol (1)](image)

Off-white powder, m.p. 220 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.43 (s, 9H), 3.77 (s, 3H), 5.04 (s, 1H), 6.62 (d, 1H, J = 3.0 Hz), 6.96(d, 1H, J = 3.0 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.5, 35.2, 55.7, 111.8, 115.3, 123.3, 138.9, 145.9, 153.2.

3,3'-di-tert-butylbiphenyl-2,2',5,5'-tetraol (2)

![Structure of 3,3'-di-tert-butylbiphenyl-2,2',5,5'-tetraol (2)](image)

White chalky solid, m.p. 222 °C; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 1.36 (s, 9H), 6.49 (d, 1H, J = 2.9 Hz), 6.68 (d, 1H, J = 2.9 Hz), 8.39 (s, 1H), 8.86 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 30.3, 35.1, 113.6, 115.4, 131.6, 140.8, 144.1, 151.4.

5,5'-di-tert-butyl-6,6'-dihydroxybiphenyl-3,3'-diyl bis(trifluoromethanesulfonate) (3)

![Structure of 5,5'-di-tert-butyl-6,6'-dihydroxybiphenyl-3,3'-diyl bis(trifluoromethanesulfonate) (3)](image)

Gummy liquid; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.45 (s, 9H), 5.44 (s, 1H), 7.04 (d, 1H, J = 3.1 Hz), 7.30 (d, 1H, J = 3.1 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 29.2, 35.5, 118.8 (q, J = 320.0 Hz), 121.2, 121.8, 122.5, 140.6, 142.9, 151.7.
6,6′-diacetyl-5,5′-di-tert-butylbiphenyl-3,3′-diyl bis(trifluoromethanesulfonate) (4)

[Diagram of compound 4]

a white solid, m.p. 109 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.38 (s, 9H), 1.85 (s, 3H), 7.06 (d, 1H, $J$ = 2.9 Hz), 7.36 (d, 1H, $J$ = 3.1 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.4, 29.9, 35.2, 118.8 (q, $J$ = 321.0 Hz), 120.9, 122.4, 133.6, 144.9, 146.4, 146.6, 167.9.

3,3′-di-tert-butyl-5,5′-divinylbiphenyl-2,2′-diacetate (5)

[Diagram of compound 5]

a white solid, m.p. 118 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.38 (s, 9H), 1.84 (s, 3H), 5.22 (d, 1H, $J$ = 11.2 Hz), 5.70 (dd, 1H, $J_1$ = 17.6 Hz, $J_2$ = 0.6 Hz), 6.70 (dd, 1H, $J_1$ = 17.6 Hz, $J_2$ = 10.9 Hz), 7.24 (d, 1H, $J$ = 1.9 Hz), 7.41 (d, 1H, $J$ = 2.1 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.8, 30.4, 34.7, 114.0, 125.0, 127.9, 133.4, 135.4, 136.4, 141.3, 146.4, 168.6.

3,3′-di-tert-butyl-5,5′-divinylbiphenyl-2,2′-diol (6)

[Diagram of compound 6]

a white solid, m.p. 55 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.45 (s, 9H), 5.14 (d, 1H, $J$ = 10.9 Hz), 5.30 (s, 1H), 5.62 (d, 1H, $J$ = 17.6 Hz), 6.66 (dd, 1H, $J_1$ = 17.6 Hz, $J_2$ = 11.0 Hz), 7.16 (d, 1H, $J$ = 1.8 Hz), 7.42 (d, 1H, $J$ = 1.6 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 29.5, 35.0, 112.0, 122.5, 126.2, 126.3, 130.2, 136.3, 137.3, 152.0.

2,2′-bisphenoxyphosphorus chloride (7)

[Diagram of compound 7]

yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, 2H, $J$ = 7.9 Hz), 7.31 (t, 2H, $J$ = 7.4 Hz), 7.37 (td, 2H, $J_1$ = 7.7 Hz, $J_2$ = 1.6 Hz), 7.46 (dd, 2H, $J_1$ = 7.5 Hz, $J_2$ = 1.6 Hz); $^{31}$P NMR (100 MHz, CDCl$_3$) δ 122.2 (d, $J$ = 1.9 Hz), 126.2, 129.4, 130.1, 130.9 (d, $J$ = 3.5 Hz), 149.2 (d, $J$ = 5.7 Hz); $^{31}$P NMR (161.8 MHz, CDCl$_3$) δ 179.4.
6,6’-(3,3’-di-tert-butyl-5,5’-divinylbiphenyl-2,2’ diyl)bis(oxy)didibenzo[1,3,2]dioxaphosphepine (A)

da white solid, m.p. 185°C; \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.32 (s, 9H), 5.24 (dd, 1H, \(J_1 = 10.9\) Hz, \(J_2 = 0.5\) Hz), 5.74 (dd, 1H, \(J_1 = 17.6\) Hz, \(J_2 = 0.5\) Hz), 6.75 (dd, 1H, \(J_1 = 17.6\) Hz, \(J_2 = 10.9\) Hz), 6.72 (d, 1H, \(J = 7.6\) Hz), 7.01 (td, 1H, \(J_1 = 7.9\) Hz, \(J_2 = 1.3\) Hz), 7.10-7.15 (m, 2H), 7.23 (td, 1H, \(J_1 = 7.5\) Hz, \(J_2 = 1.2\) Hz), 7.29 (td, 1H, \(J_1 = 7.8\) Hz, \(J_2 = 1.8\) Hz), 7.35 (dd, 1H, \(J_1 = 7.7\) Hz, \(J_2 = 1.6\) Hz), 7.39-7.44 (m, 2H), 7.54 (d, 1H, \(J = 2.3\) Hz); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 30.4, 35.3, 113.4, 122.3, 123.1, 124.8, 124.9, 126.1, 128.7, 128.8, 129.4, 129.6, 129.8, 131.2, 131.3, 131.5, 132.5, 136.4, 141.9, 149.0, 149.7, 150.2; \(^{31}P\) NMR (161.8 MHz, CDCl\(_3\)) \(\delta\) -6.8; HRMS (ESI): m/z calc. for C\(_{48}\)H\(_{44}\)O\(_6\)P\(_2\) [M+H]\(^+\) : 779.2686, found: 779.2697.

tris(4-vinphenyl)phosphane (B)

da white solid, m.p. 75°C; \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.26 (d, 1H, \(J = 11.1\) Hz), 5.76 (d, 1H, \(J = 17.5\) Hz), 6.69 (dd, 1H, \(J_1 = 17.6\) Hz, \(J_2 = 10.9\) Hz), 7.25-7.29 (m, 2H), 7.35-7.37 (m, 2H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 114.7, 126.3 (d, 6C, \(J = 7.0\) Hz), 133.8 (d, 3C, \(J = 19.4\) Hz), 136.3, 136.6 (d, 6C, \(J = 10.8\) Hz), 137.9; \(^{31}P\) NMR (161.8 MHz, CDCl\(_3\)) \(\delta\) -6.8;

**NMR spectra of compounds 1-7 and A, B**
500 MHz, CDCl₃

125 MHz, CDCl₃