Single atom dispersed Rh-Biphephos&PPh$_3$@porous organic copolymers：Highly efficient catalysts for continuous fixed-bed hydroformylation of propene

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1. Supporting Figures

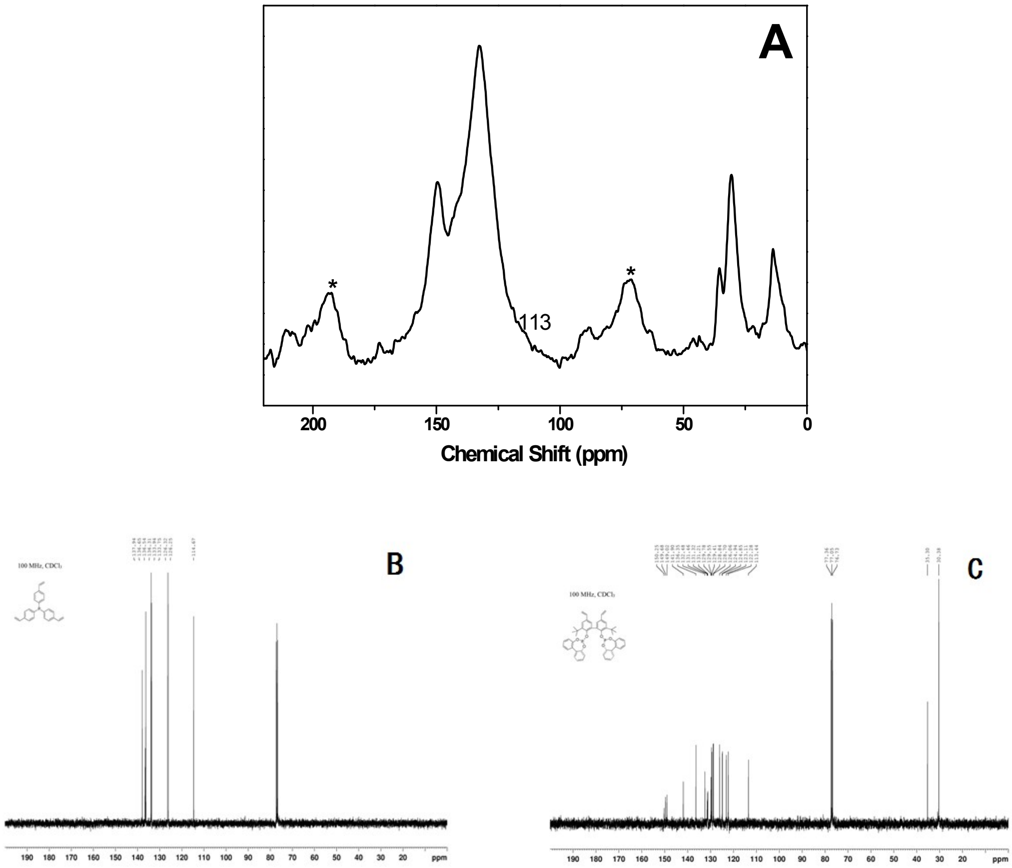


Figure S1. (A) ^{13}C MAS NMR spectrum of CPOL-1bp&10P, (B) ^{13}C NMR spectrum of tris(4-vinphenyl)phosphane and (C) ^{13}C NMR spectrum of vinyl biphephos.

The peaks at 113 ppm in CPOL-1bp&10P, which can be assigned to unpolymerized vinyl groups, is quite small compared with the corresponding monomers (B, C), indicating that CPOL-bp&PPh$_3$-1 has high degree of polymerization. The peaks at * are side bands.

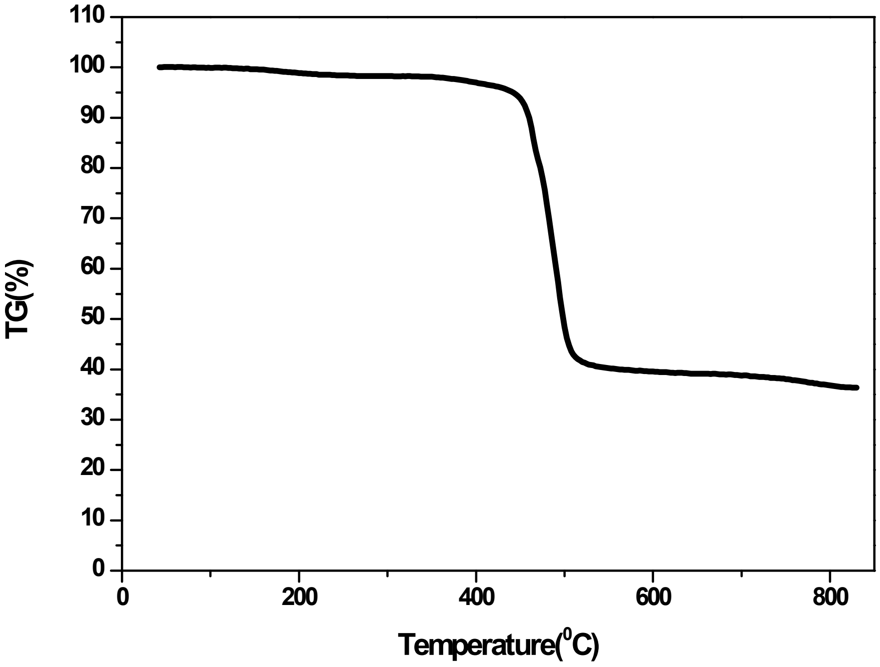
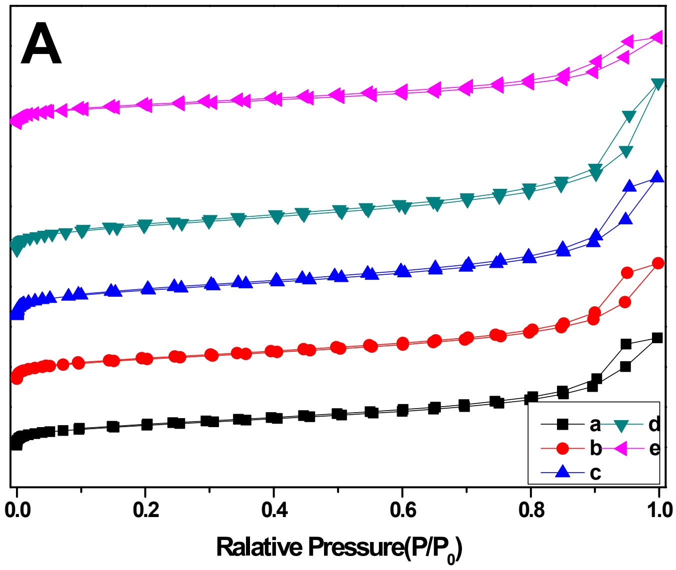


Figure S2. Thermogravimetric analysis (TGA) of CPOL-1bp&10P



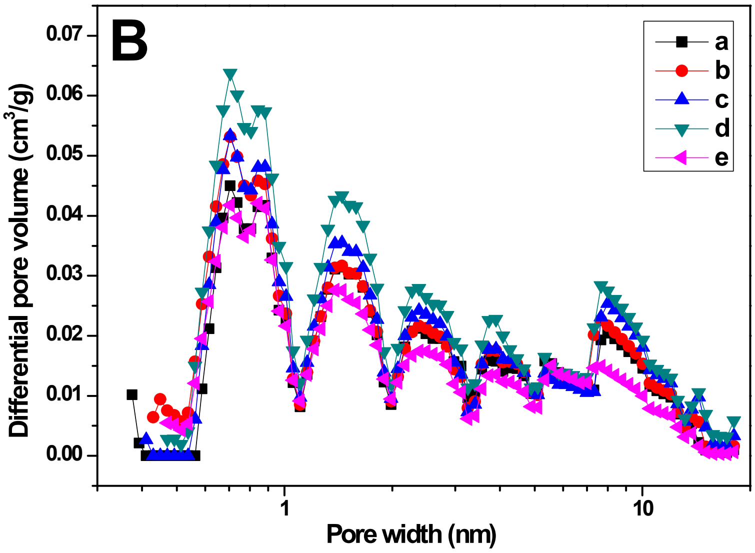
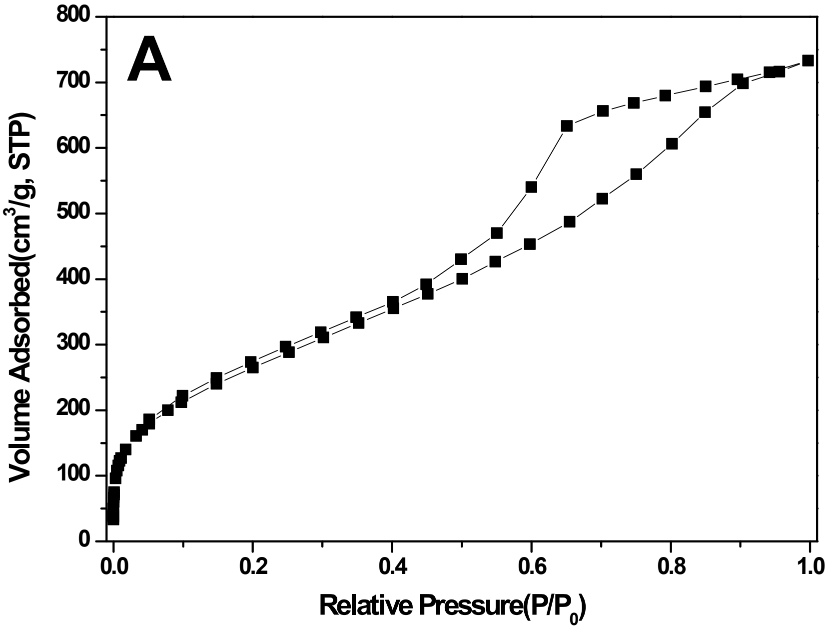


Figure S3. (A) N_2 sorption isotherms and (B) pore sizes distributions of different Rh/CPOL-bp&P catalysts: (a) 0.130 wt % Rh/CPOL-0.5bp&10P, (b) 0.130 wt % Rh/CPOL-1bp&10P, (c) 0.130 wt % Rh/CPOL-2bp&10P, (d) 0.130 wt % Rh/CPOL-3bp&10P, (e) 0.130 wt % Rh/CPOL-3.75bp&10P.



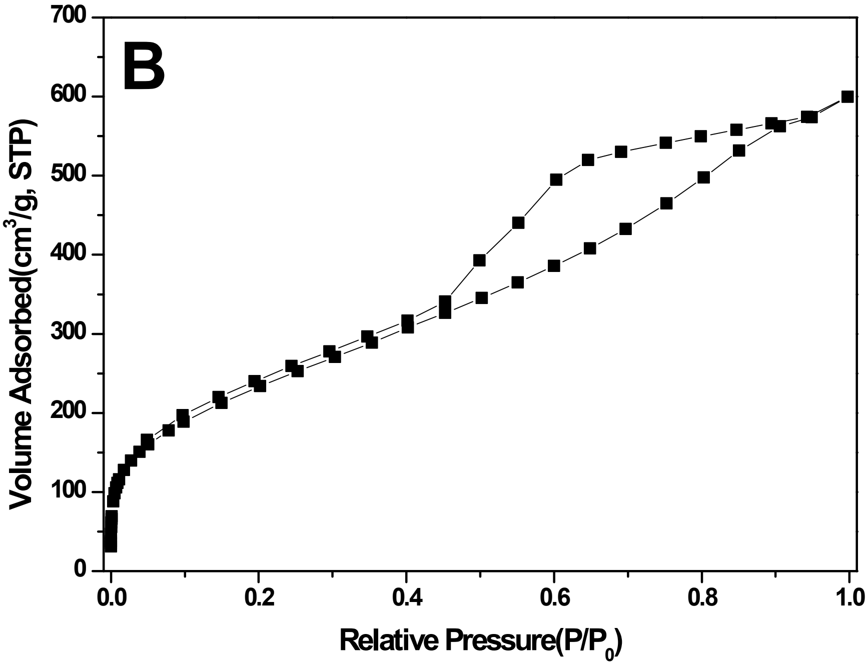


Figure S4. N_2 sorption isotherms of (A) CPOL-bp&DVB and (B) 0.130 wt % Rh/CPOL-bp&DVB. BET surface area of (A) and (B) were 973.1 and 845.3 m^2/g. The total pore volume of (A) and (B) were 1.14 and 0.93 cm^3/g.

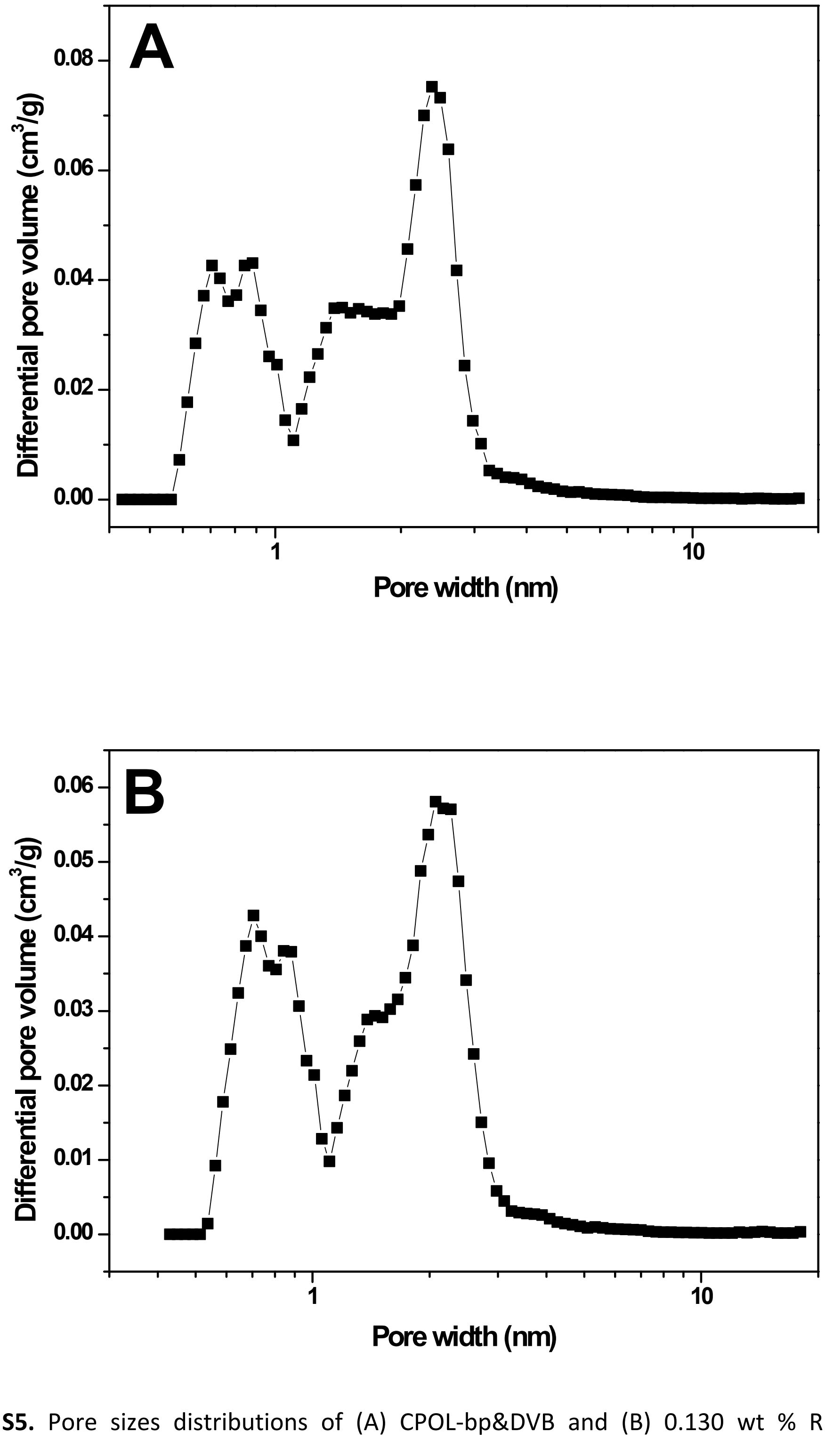


Figure S5. Pore sizes distributions of (A) CPOL-bp&DVB and (B) 0.130 wt % Rh/CPOL-bp&DVB.

Compared with CPOL-bp&P polymers, the CPOL-bp&DVB sample did not possess hierarchical porosity, which is not beneficial for substrates diffusion.

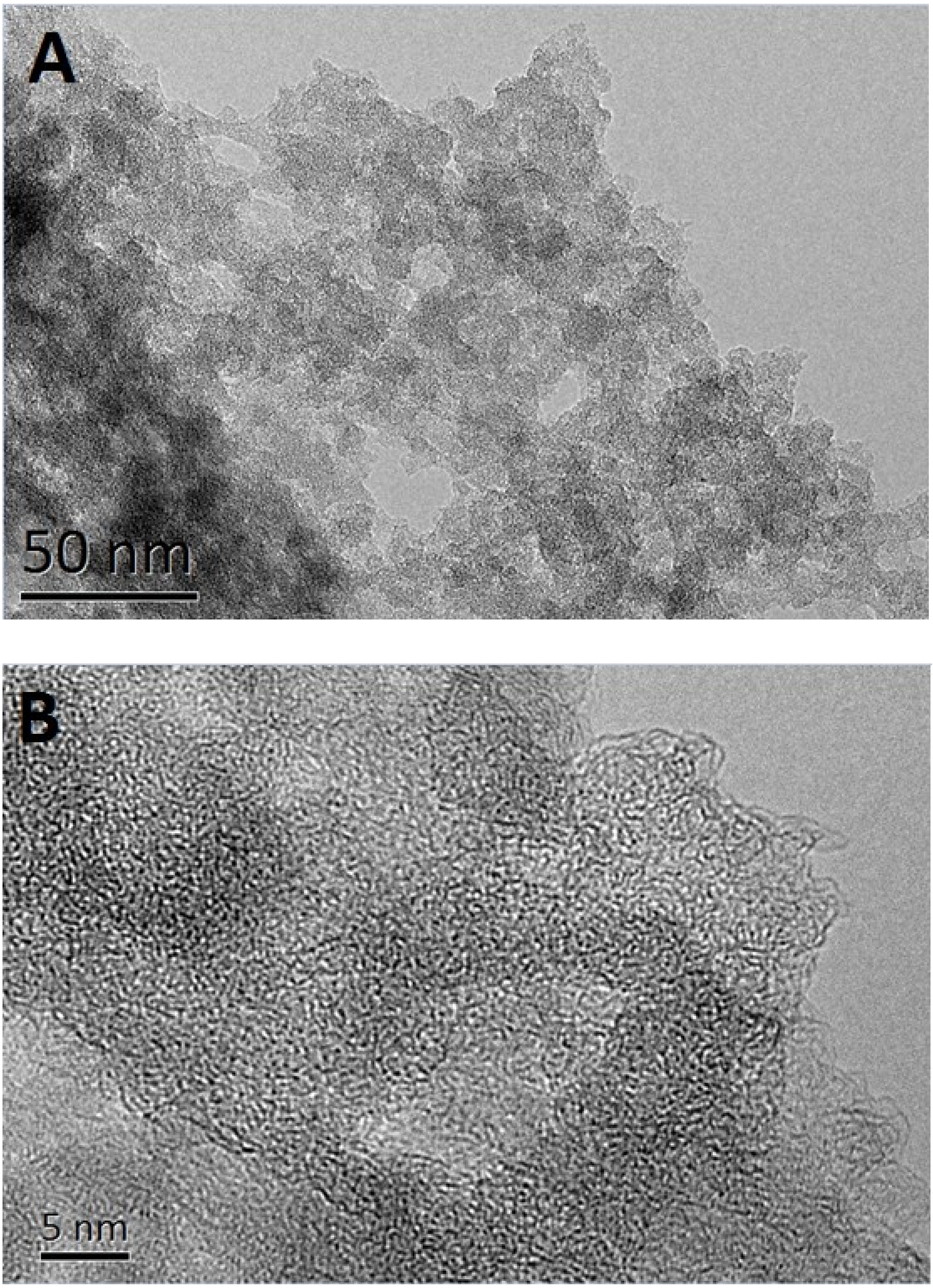


Figure S6. TEM images of CPOL-1bp&10P.

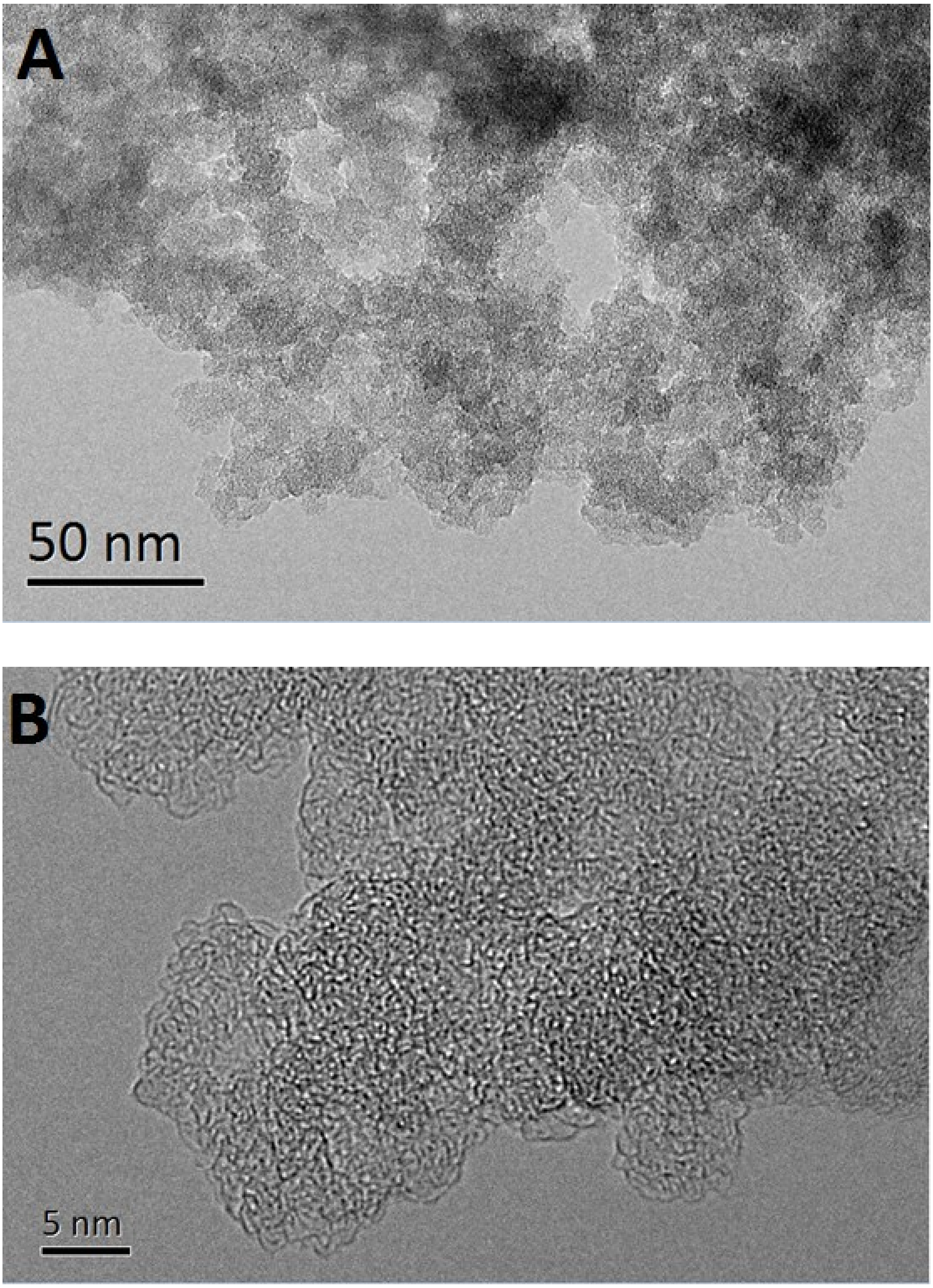


Figure S7. TEM images of 0.130 wt % Rh/CPOL-1bp&10P.

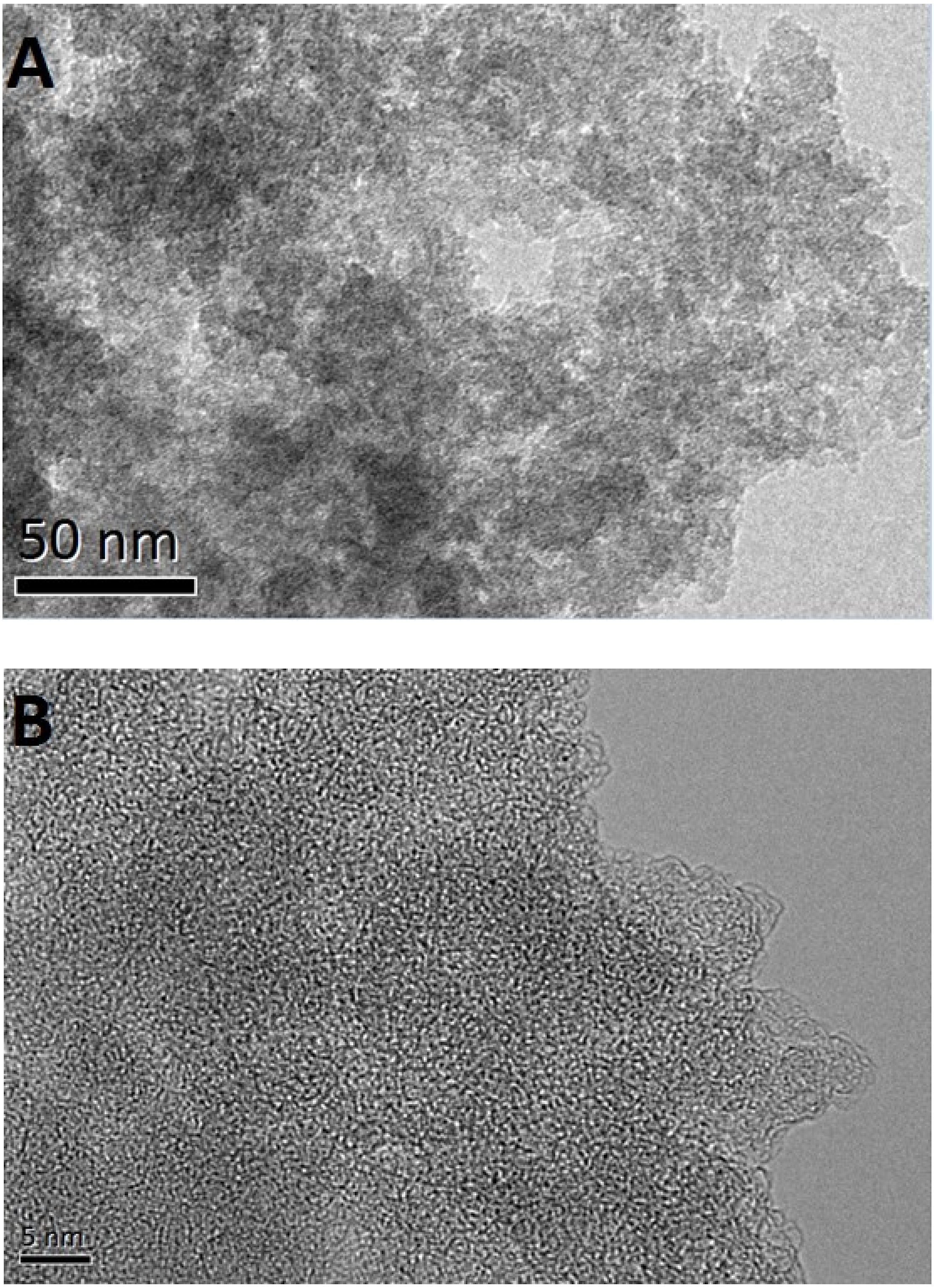
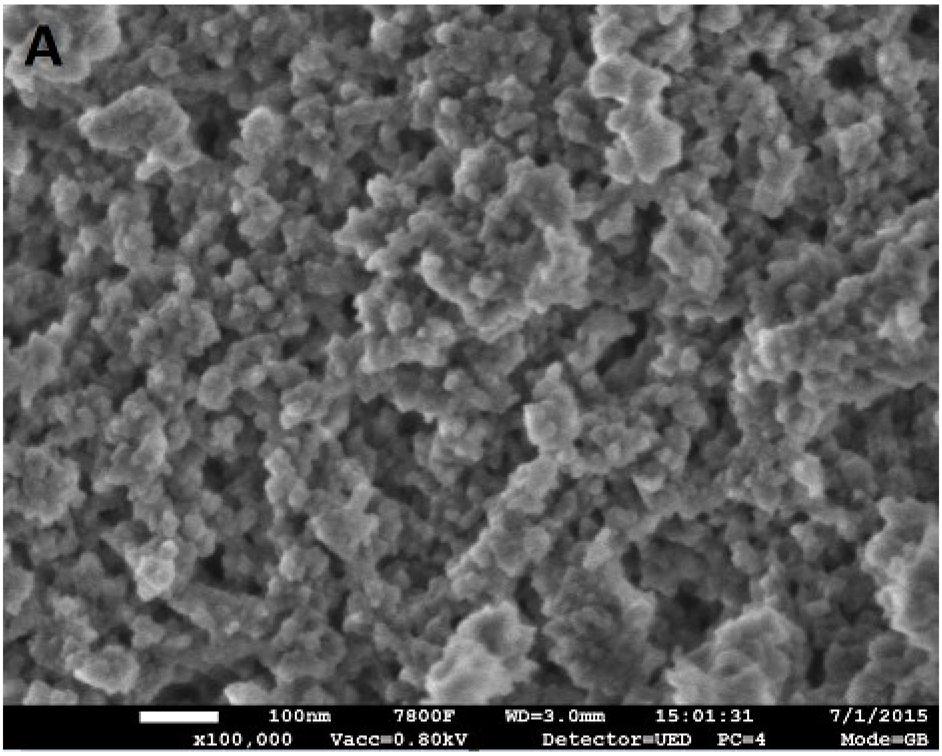


Figure S8. TEM images of 0.130 wt % Rh/CPOL-1bp&10P after time on stream of 1000 hours.

TEM images show that rhodium nanoparticles cannot be detected from both fresh 0.130 wt % Rh/CPOL-1bp&10P and spent 0.130 wt % Rh/CPOL-1bp&10P catalyst after after time on stream of 1000 hours, indicating that high dispersion of rhodium on the surfaces of samples.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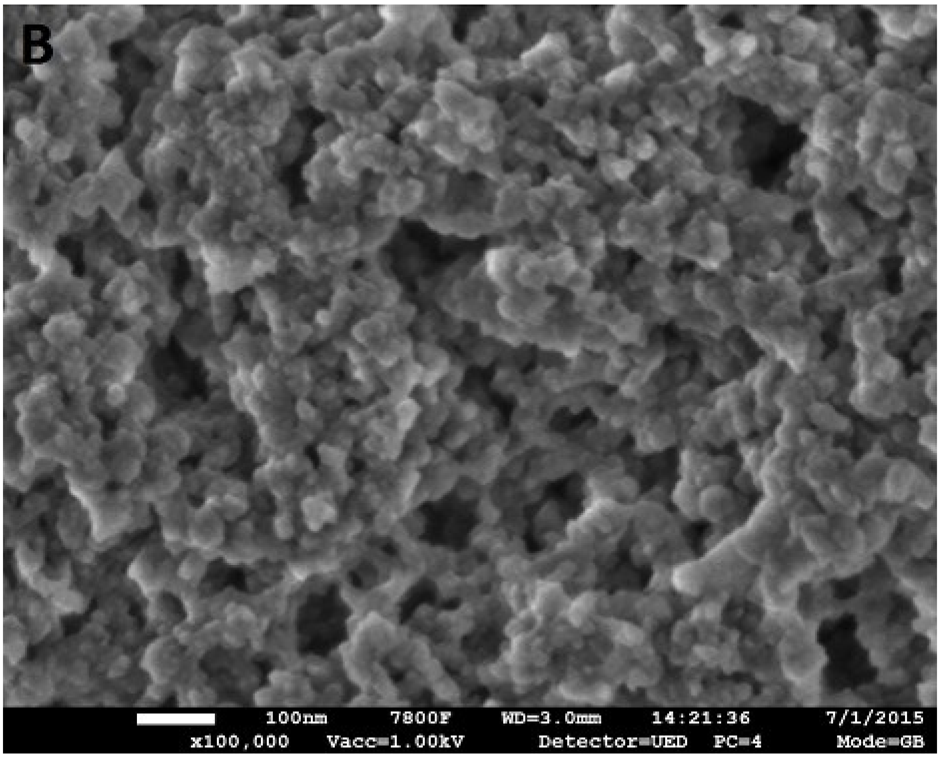
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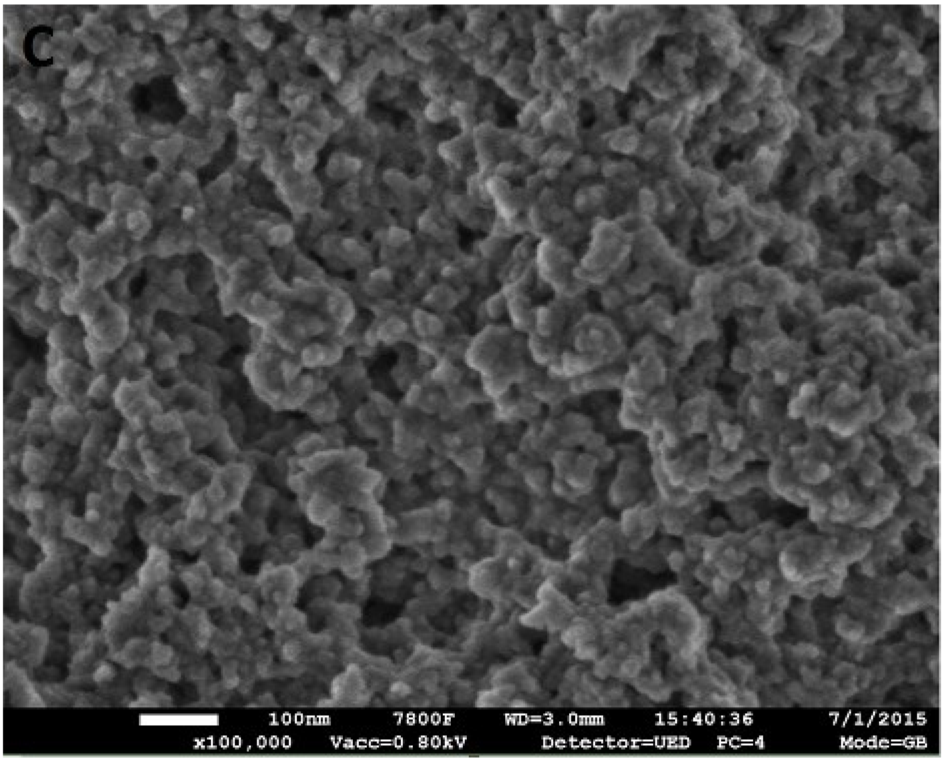
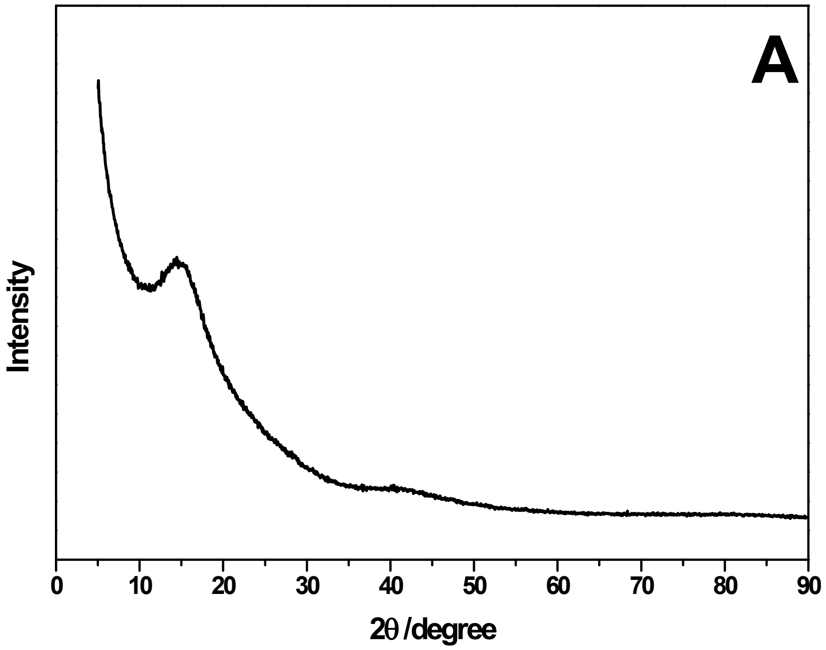


Figure S9. SEM images of (A) CPOL-1bp&10P, (B) 0.130 wt % Rh/CPOL-1bp&10P and (C) 0.130 wt % Rh/CPOL-1bp&10P after time of stream of 1008 hours.

Figure S9 shows that the all the samples have hierarchical porosity.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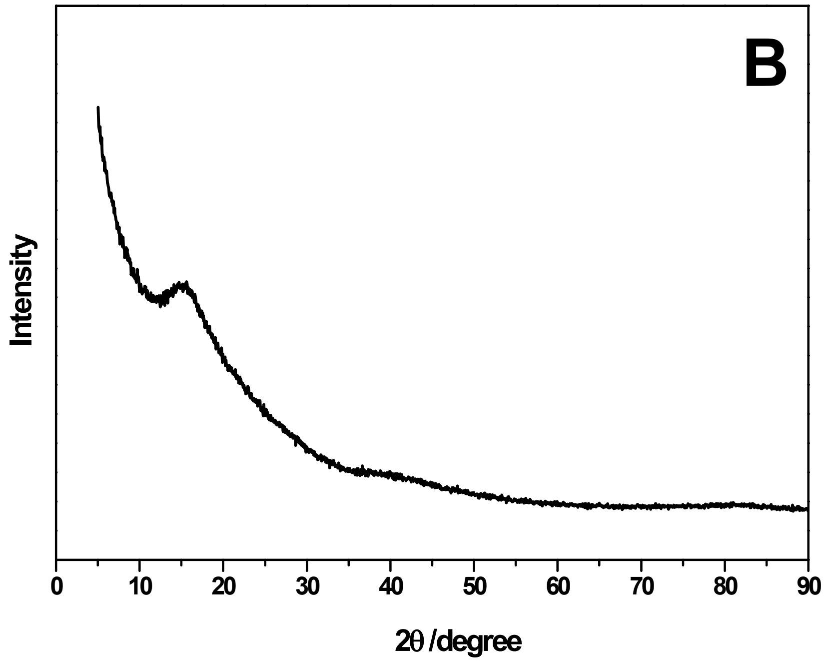
2θ /degree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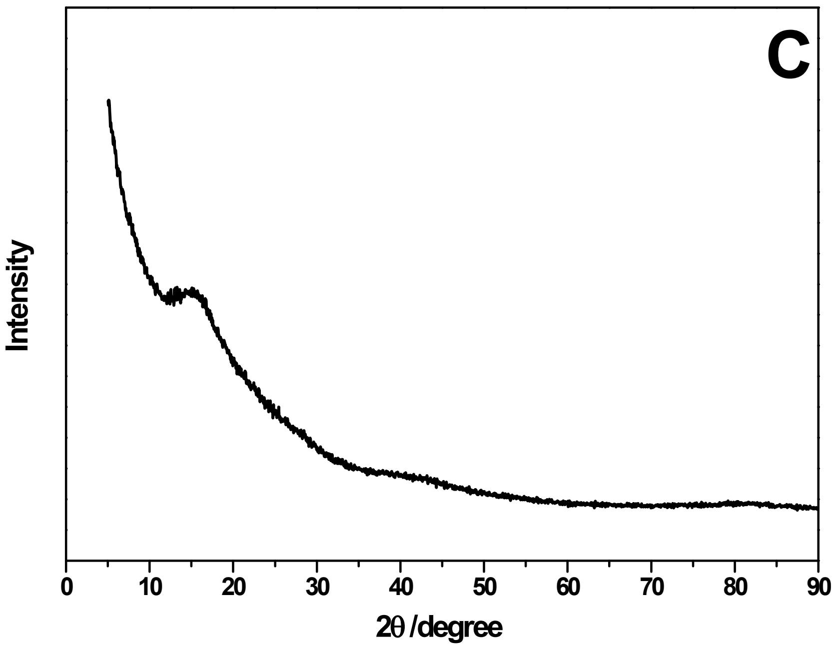

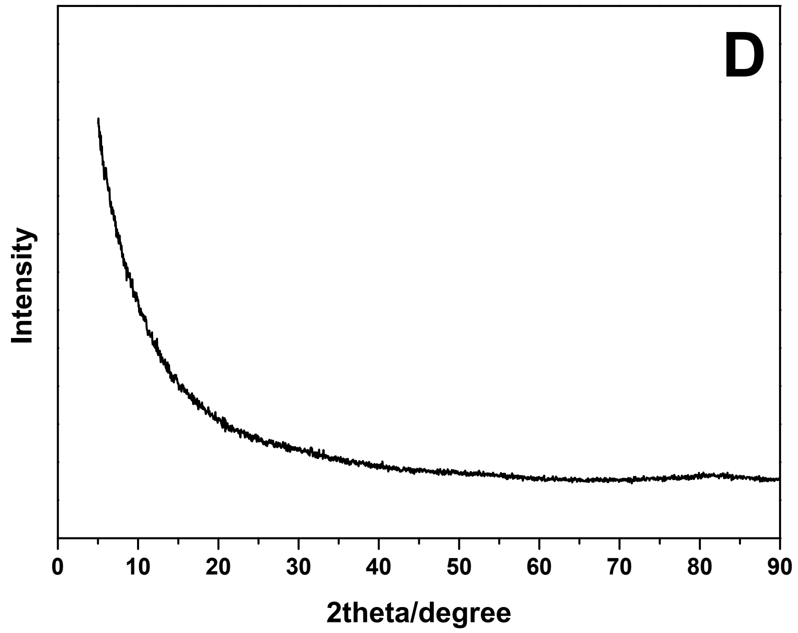

Figure S10. XRD of (A) CPOL-1bp&10P, (B) 0.130 wt % Rh/CPOL-1bp&10P, (C) 0.130 wt % Rh/CPOL-1bp&10P after time of stream of 1008 hours and (D) Silicon substraat sample stage.

XRD also show that rhodium nanoparticles cannot be detected from both fresh 0.130 wt % Rh/CPOL-1bp&10P and spent 0.130 wt % Rh/CPOL-1bp&10P after time on stream of 1008 hours, indicating that high dispersion of rhodium on the surfaces of samples. All three samples are amorphous according to XRD data.

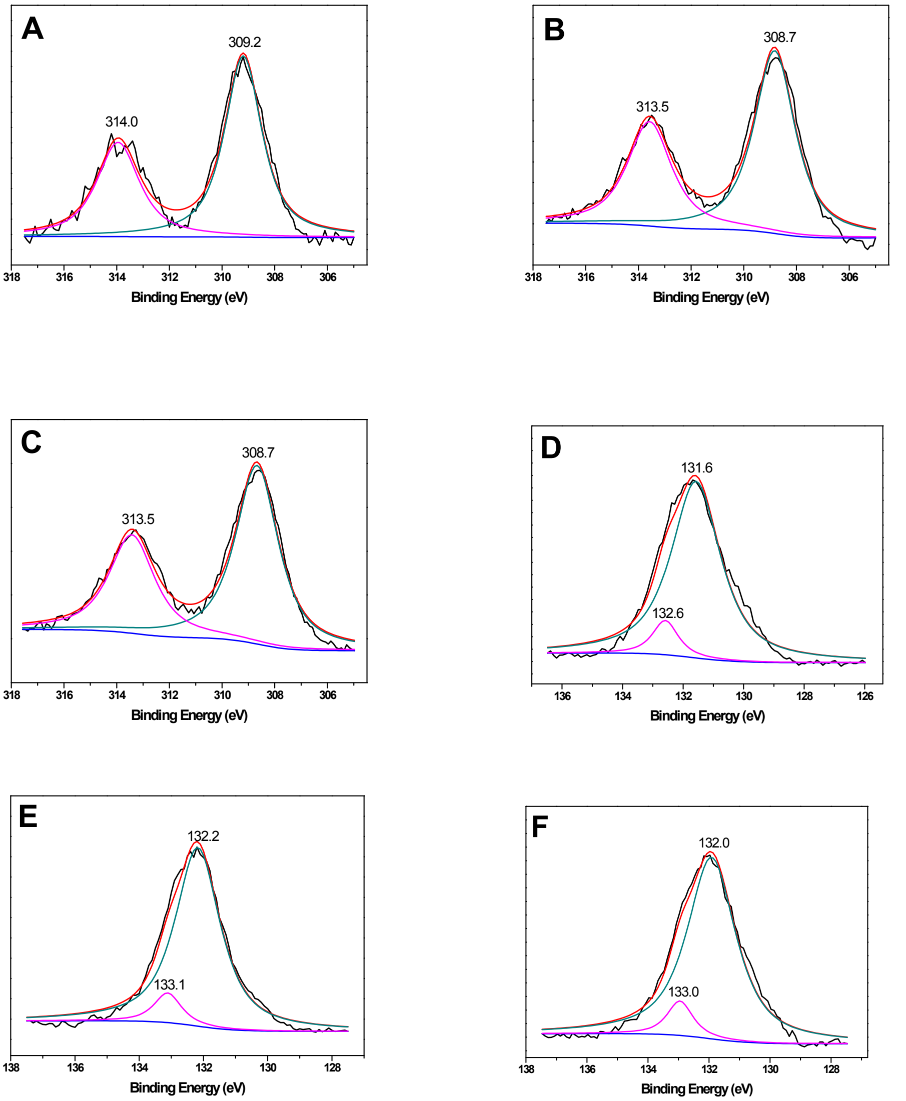

Figure S11. (A) Rh3d XPS spectra of Rh(CO)$_2$(acac), (B) Rh3d XPS spectra of 0.130 wt % Rh/CPOL-1bp&10P, (C) Rh3d XPS spectra of 2.0 wt % Rh/CPOL-1bp&10P, (D) P2p XPS spectra of CPOL-1bp&10P, (E) P2p XPS spectra of 0.130 wt % Rh/CPOL-1bp&10P, (F) P2p XPS spectra of 2.0 wt % Rh/CPOL-1bp&10P.

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 0.13% Rh/CPOL-1bp&10P catalyst, the binding energies of Rh3d$_{3/2}$ and Rh3d$_{5/2}$ decrease to 313.5 eV and 308.7 eV, showing the successful coordination of Rh(CO)$_2$(acac) with CPOL-1bp&10P carrier. Interestingly, compared with XPS spectra of P2p in CPOL-1bp&10P (two kinds of P species: PPh$_3$ units at 131.6 eV, biphphos units at 132.6 eV), 0.13% Rh/CPOL-bp&PPh3-1 give relatively higher binding energy (132.2 eV, 133.3 eV), indicating the successful coordination of Rh with two kinds of P species in the polymer skeleton. The same phenomena can be observed in 2.0% Rh/CPOL-1bp&10P catalyst.

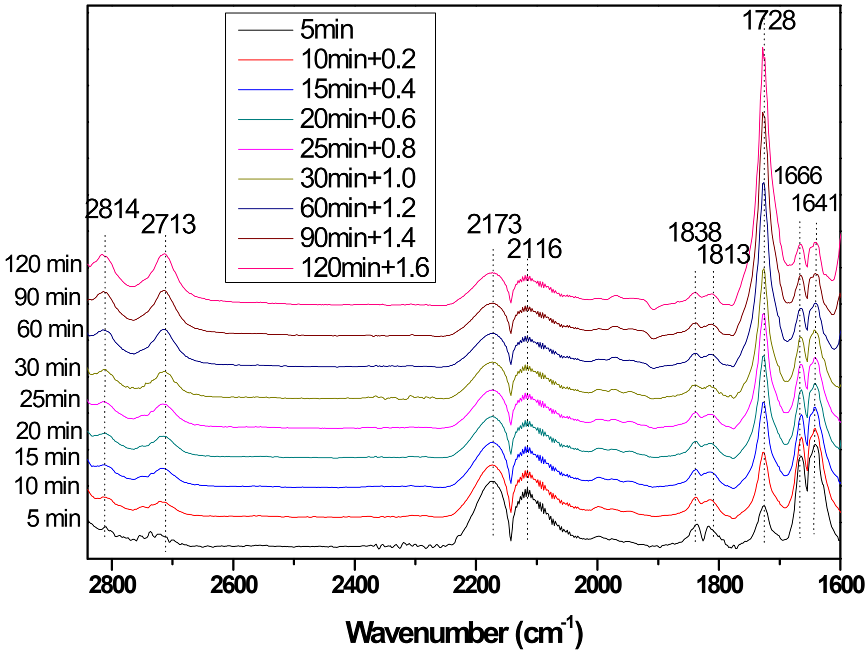

Figure S12. In situ FT-IR spectra of the 0.130 wt % Rh/CPOL-1bp&10P catalyst.

In situ FT-IR spectra were measured on a Bruker Nicolet iS50 Fourier transform infrared spectrometer in the range 400-4000cm^{-1}. All specters were recorded with 32 scans with a resolution of 4 cm^{-1}. The sample was purified in a flow of N_2 at 70 °C for 60 min and then a premixed gas (C_3H_6:CO:H_2 =1:1:1) was introduced for 120 min under atmospheric pressure.

The peaks at 1728 cm^{-1} resulted from the stretching vibration of C=O in butaldehyde and two peaks at 2713 cm^{-1} and 2814 cm^{-1} due to the stretching vibration of C-H in butaldehyde. The 2116 and 2173 cm^{-1} can be ascribed to CO gas. The 1641, 1666, 1813 and 1838 cm^{-1} resulted from propene.

From the in situ FT-IR spectra, we can see that even under a very mild conditions (70 °C, atmospheric pressure), the propene can be converted to butaldehyde quickly using Rh/CPOL-1bp&10P catalyst, indicating the high efficiency of the Rh/CPOL-1bp&10P catalyst.

2. Supporting Tables

Table S1. Influence of the ratio of vinyl biphephos:3vPPh$_3$ on the Surface area and pore volume of the obtained polymers

Samples	vinyl biphephos：3vPPh$_3$	BET Surface Area/ m^2·g^{-1}	Pore Volume/ cm^3·g^{-1}
Rh/CPOL-0.5bp&10P	0.021869	978.4	2.11
Rh/CPOL-1bp&10P	0.043738	1059	2.32
Rh/CPOL-2bp&10P	0.087476	1105	2.67
Rh/CPOL-3bp&10P	0.131215	1300	3.32
Rh/CPOL-3.75bp&10P	0.164018	844.3	1.71

Table S2. Comparation of concentration of exposed P in CPOL-1bp&10P and CPOL-bp&DVB.

Samples	Rh content(wt.%)
Rh/CPOL-1bp&10P (after washing)	5.49%
Rh/CPOL-bp&DVB (after washing)	0.712%

To test the concentration of exposed P in CPOL-1bp&10P and CPOL-bp&DVB, 0.2g of CPOL-1bp&10P and CPOL-bp&DVB samples were soaked with 5ml of THF solution containing 0.15g of Rh(CO)$_2$(acac) respectively. After stirring for 24 h under N$_2$ atmosphere at room temperature, the samples were filtrated and washed with THF using Soxhlet extraction for 24h, then the THF was evaporated at 65 ^{o}C under vacuum. Thus the remaining Rh was all coordinated with P atoms in the polymer skeleton. The metal loading was determined by inductively coupled plasma (ICP) analysis. And the metal loading can somehow reflect the concentration of exposed P in the polymer.

Table S3. Rh concentration of fresh and spend catalyst.

Samples	Rh content(wt.%)
Rh/CPOL-1bp&10P (fresh sample)	0.130%
Rh/CPOL-1bp&10P (spend sample, 1008 hours)	0.131%

We also have concentrated the solution in the condenser and the ICP-AES test of concentrated solution shows that the Rh species are undetectable. This gives further evidence that the leaching of Rh species can be neglected.

Table S4. P concentration of fresh and spend catalyst.

Samples	P content (wt.%)
Rh/CPOL-1bp&10P (fresh sample)	8.94%
Rh/CPOL-1bp&10P (spend sample, 1008 hours)	8.95%