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# Ultrastable 3V-PPh<sub>3</sub> polymers supported single Rh sites for fixed-bed hydroformylation of olefins



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#### ABSTRACT

The heterogenization of homogeneous catalysts is of critical importance for both fundamental research and practical applications. The key obstacle to industrial applications of heterogenized homogeneous catalysts is the long-term stability of the immobilized molecular complexes. We unambiguously demonstrate in this report that the vinyl-functionalized PPh<sub>3</sub> polymers supported single Rh sites (Rh/POL–PPh<sub>3</sub>) catalyst provided not only excellent catalytic activity but also ultrahigh stability for fixed-bed olefins hydroformylation, which is one of the most important industrial homogeneous catalytic processes for the synthesis of aldehydes and alcohols. HAADF-STEM and EXAFS results indicated that the Rh atoms were present in single Rh sites which were strongly coordinated with the exposed phosphorous atoms of the POL–PPh<sub>3</sub> support. The Rh/POL-PPh<sub>3</sub> catalyst provided high activity and selectivity because it maintained the catalytic functionalities similar to the homogeneous HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> complex, as demonstrated both by <sup>31</sup>P MAS NMR and in situ FT-IR experiments. Thus a reaction mechanism, similar to that over the homogeneous HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> complex, was proposed for olefin hydroformylation over the novel Rh/POL–PPh<sub>3</sub> catalyst.

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# 1. Introduction

Homogeneous catalysts possess high activity and selectivity due to their well-defined and uniform single active sites but suffer the problem of catalyst recyclability [1]. Heterogeneous catalysts, on the other hand, exhibiting relatively low activity and selectivity, usually consist of solids which can be easily separated and recycled [2]. Therefore, heterogenization of homogeneous catalysts by anchoring the active molecular complexes is expected to provide catalytic systems that combine the advantages of both homogenous and heterogeneous catalysts [3–15]. For this purpose, many different approaches have been explored. Well-known strategies for immobilizing active molecular complexes in the past decades include: (1) grafting molecular complexes to polymer resins or inorganic oxides [6,7], (2) immobilizing them on porous materials

\* Corresponding authors at: Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, China. Tel.: +86 411 84379143; fax: +86 411 84379143. by covalent linking through aliphatic phosphorus or amine-based spacer [12], (3) in situ formation of Rh–P complexes on the surfaces of heterogeneous catalysts [9,10,16,17]. These approaches not only focus on reutilization of the catalysts but also on the potential enhancement of their activity and selectivity. The long-term stability of the immobilized molecular species, however, has been a key issue to be solved [18,19].

Hydroformylation of olefins is believed to be one of the most widely used industrial homogeneous catalytic processes for the synthesis of aldehydes and alcohols (more than 8,000,000 t annually) [20,21]. Extensive research has been performed with the goal of developing stable heterogenized homogeneous catalysts for hydroformylation. However, limited success has been achieved, resulting in lack of industrial practice with such catalysts. Although our group [17] previously developed highly stable heterogenized catalysts for hydroformylation but their activity is relatively poor.

The application of porous organic polymers (POPs) in heterogeneous catalysis have attracted many scientists attention due to their remarkable properties such as high surface area, low skeletal density, and introducing chemical functionalities within the porous framework [2,22–24]. In our previous work, 3V-PPh<sub>3</sub> poly-

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Entry	Catalyst	Rh loading (wt%)	Conversion (%)	Selectivity (%)	TOF (h <sup>-1</sup> )
1 <sup>a</sup>	Rh/POL-PPh3	0.125	96.2	96.1	4530
2 <sup>a</sup>	Rh/POL-PPh3	0.063	65.3	96.4	6166
3 <sup>a</sup>	Rh(CO) <sub>2</sub> (acac)/SiO <sub>2</sub>	0.125	0.6	99.9	30
4 <sup>a</sup>	HRh(CO)(PPh3)3/SiO2	0.125	22.4	99.5	1091
5 <sup>b</sup>	Rh/POL–PPh <sub>3</sub>	0.125	88.8	95.4	10373
6 <sup>b</sup>	Rh/POL-PPh3	0.063	45.5	94.6	10534

Results of ethylene hydroformylation over various Rh catalysts.

<sup>a</sup> Reaction conditions: a fixed-bed reactor, P = 1.0 MPa ( $C_2H_4$ :CO:H<sub>2</sub> = 1:1:1), T = 393 K, GHSV of  $C_2H_4$ /CO/H<sub>2</sub> = 2000 h<sup>-1</sup>.

<sup>b</sup> Reaction conditions: a fixed-bed reactor, P = 1.0 MPa (C<sub>2</sub>H<sub>4</sub>:CO:H<sub>2</sub> = 1:1:1), T = 393 K, GHSV of C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> = 5000 h<sup>-1</sup>.

mer (POL–PPh<sub>3</sub>), possessing high thermal stability, high BET surface area and hierarchical porosity, was synthesized through solvothermal polymerization of vinyl-functionalized PPh<sub>3</sub> (3V-PPh<sub>3</sub>), and supported Rh/POL–PPh<sub>3</sub> catalyst has been developed for hydroformylation of 1-octene with excellent performance [25]. However, the chemical nature and structure property of the Rh/POL–PPh<sub>3</sub> catalyst have not been understood profoundly, owing to characterizing amorphous non-soluble POPs immobilized metal species catalysts is definitely the greatest challenge in POP-based catalysis nowadays [23,24]. Hence a lot of work is required to comprehensively understand the structure-property-activity relations with the Rh/POL–PPh<sub>3</sub> catalyst.

In the present work, we further investigate the state of metal species and the coordination behaviors between metal species and phosphine species in POL–PPh<sub>3</sub> over the Rh/POL–PPh<sub>3</sub> catalyst, by HAADF-STEM, EXAFS, <sup>31</sup>P MAS NMR and in situ FT-IR techniques, to elucidate the reason for its high activity and selectivity. With the purpose of testing the practice application of the Rh/POL–PPh<sub>3</sub> catalyst, long-term stabilities in ethylene and 1-dodecene hydro-formylation reaction were carried out in a fixed-bed reactor instead of an autoclave reactor.

# 2. Experimental

All materials handling, preparations and manipulations were carried out under N<sub>2</sub> either in a glove-box or using standard Schlenk techniques.

# 2.1. Materials

1-dodecene substrates (95%) were purchased from Aladdin Company, Co. Ltd. The  $Rh(CO)_2(acac)$  and  $HRh(CO)(PPh_3)_3$  were purchased from J&K Scientific Ltd. A commercial SiO<sub>2</sub>, from Qingdao Haiyang Chemicals Plant, was used as support materials. Tetrahy-



**Fig. 1.** Stability test of the 0.125 wt% Rh/POL–PPh<sub>3</sub> catalyst for hydroformylation of ethylene. Reaction conditions: a fixed-bed reactor, P = 1.0 MPa (C<sub>2</sub>H<sub>4</sub>:CO:H<sub>2</sub>=1:1:1), T = 393 K, GHSV = 2000 h<sup>-1</sup>.

drofuran (A.R.) and toluene (A.R.) were refluxed with sodium under  $N_2$  for deoxygenation and dehydration.

#### 2.2. Preparations of the catalysts

POL-PPh<sub>3</sub> was prepared according to the method reported previously [25]. Rh/POL-PPh<sub>3</sub> and HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/POL-PPh<sub>3</sub> catalysts were prepared, respectively. 1.2 g POL-PPh<sub>3</sub> was added to 100 mL THF containing 3.8 mg Rh(CO)<sub>2</sub>(acac) or 214 mg HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> and the resulting solution was stirred at room temperature for 24 h under N<sub>2</sub>. The final catalyst was centrifugally separated, washed with excessive THF and dried at 333 K under vacuum. The loading level of the Rh prior to and after the hydroformylation reaction was determined by the inductively coupled plasma (ICP) method.

# 2.3. Catalysts characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a JEOL JEM-ARM200F equipped with a CEOS probe corrector, with a guaranteed resolution of 0.08 nm. Rh K-edge X-ray absorption fine structure (EXAFS and XANES) spectra of the prepared catalysts were obtained at the BL14W1 beamline of SSRF, SINAP (Shanghai, China) with the use of a Si(311) crystal monochromator. The storage ring was operated at 3.5 GeV with injection currents of 200 mA. Rh foil was used as reference samples, and all the X-ray absorption spectra were measured in the transmission mode. All spectra of the assynthesized catalysts were conducted in the fluorescence mode. The raw data were energy-calibrated (Rh K-edge energy of Ru foil) at 23,220 eV, first inflection point, background-corrected, and normalized using the IFEFFIT software. Fourier transformation of the EXAFS data was applied to the  $k^3$ -weighted functions. For the curve-fitting analysis, Rh-C and Rh-P path parameters were obtained from the ab initio multiple scattering code FFEF6. Solidstate <sup>31</sup>P 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 10kHz and a delay of 3.0s. Solidstate <sup>31</sup>P NMR chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub>. In situ FT-IR spectra were measured on a Bruker Tensor 27 Fourier transform infrared spectrometer in the range 4000–400 cm<sup>-1</sup>. All spectra were recorded with 32 scans with a resolution of 4 cm<sup>-1</sup>. The sample was purified in a flow of  $N_2$  at 393 K for 60 min and then a premixed gas  $(C_2H_4:CO:H_2 = 1:1:1)$  was introduced for 60 min under atmospheric pressure. The spectrum was recorded after purging the chamber with N<sub>2</sub> for 30 min. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on an IRIS Intrepid II XSP instrument (Thermo Electron Corp.).

# 2.4. Catalytic activity tests

The hydroformylation of ethylene was conducted in a continuous flow fixed-bed reactor with an inner diameter of 9 mm. The

Table 1



**Fig. 2.** HAADF-STEM images of Rh/POL–PPh<sub>3</sub> catalysts: (a) 0.125 wt% Rh/POL–PPh<sub>3</sub> sample before reaction; (b) the same catalyst after 1008 h of time-on-stream for ethylene hydroformylation; (c–d) 2.0 wt% Rh/POL–PPh<sub>3</sub> catalyst after 504 h for ethylene hydroformylation. Isolated single Rh atoms are clearly shown in both the fresh and the used catalysts with uniform distribution throughout the porous POL–PPh<sub>3</sub> support.

effluent was passed through a condenser filled with 60 mL of cold de-ionized water. Propanal was captured by dissolution into the water in the condenser. The aqueous solution containing propanal was analyzed off-line with an Agilent 7890A gas chromatography, using an FID and ethanol as an internal standard. The tail gas was analyzed on-line using an Agilent 7890A gas chromatography with a Porapak-QS column and a TCD.

The hydroformylation of 1-dodecene was conducted in a tricklebed reactor with an inner diameter of 9 mm. The products of hydroformylation were analyzed by an Agilent 7890A gas chromatography, using an FID and *n*-propanol as an internal standard.

# 3. Results and discussion

#### 3.1. Hydroformylation results

#### 3.1.1. Hydroformylation of ethylene

To make it more feasible and practical, a fixed-bed reactor was employed in ethylene hydroformylation using the Rh/POL–PPh<sub>3</sub> catalyst of very low metal loading. A fixed-bed reactor for hydroformylation reaction is advantageous because it can make sure the catalytically active species are coming from the surface of heterogeneous catalysts rather than from the leaching of heterogeneous Rh–P complexes. The performance of various Rh



**Fig. 3.** The Rh K-edge  $k^3$ -weighted fourier transform spectra from EXAFS. (1) the used 0.125 wt% Rh/POL-PPh<sub>3</sub> sample (TOS = 1008 h); (2) the spent 2.0 wt% Rh/POL-PPh<sub>3</sub> sample (TOS = 504 h); (3) the fresh 2.0 wt% Rh/POL-PPh<sub>3</sub> sample; (4) the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> sample.



**Fig. 4.** <sup>31</sup>P MAS NMR spectra of the Rh/POL–PPh<sub>3</sub> samples: (1) the fresh 2.0 wt% Rh/POL–PPh<sub>3</sub> sample; (2) the 2.0 wt% Rh/POL–PPh<sub>3</sub> sample treated with syngas under reaction conditions (T=12h); (3) the spent 2.0 wt% Rh/POL–PPh<sub>3</sub> sample (TOS = 504 h); (4) the 2.0 wt% HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/POL–PPh<sub>3</sub> sample. Asterisks denote spinning sidebands.

catalysts is summarized in Table 1. It is amazing that the 0.125 wt% Rh/POL-PPh<sub>3</sub> catalyst led to a 96.2% conversion of ethylene and a 96.1% selectivity of propanal, and the turn-over-frequency (TOF) for propanal formation was estimated to be 4530 h<sup>-1</sup>. Meanwhile, the Rh(CO)<sub>2</sub>(acac)/SiO<sub>2</sub> and HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub> catalysts gave the TOF of 30 h<sup>-1</sup> and 1091 h<sup>-1</sup> at the same reaction conditions (Table 1). As is well known, the), a frame vibration peak of the Rh–P bonds at 506 cm<sup>-1</sup> appears [32]. Fig. 6 catalytically active species in homogeneous hydroformylation are homogeneous soluble Rh-P complexes [20]. In order to compare the catalytic performance with the Rh/POL-PPh<sub>3</sub> catalyst at the same conditions, we use SiO<sub>2</sub> supported Rh-P complexes (Rh(CO)<sub>2</sub>(acac) or HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>) as the heterogeneous catalysts. The Rh/POL-PPh<sub>3</sub> catalyst showed much better catalytic performance in comparison with SiO<sub>2</sub> supported homogeneous Rh catalyst, because the POL-PPh3 can be used as not only supports but also ligands simultaneously. When the Rh loading of the Rh/POL-PPh3 catalyst was adjusted to 0.063 wt%, a conversion of 65.3% and a TOF of  $6166 h^{-1}$  could be acquired. If gas hourly space velocity (GHSV) increased to  $5000 h^{-1}$ , the 0.125 wt% Rh/POL-PPh<sub>3</sub> catalyst exhibited a TOF of 10,373  $h^{-1}$  and the 0.063 wt% Rh/POL-PPh<sub>3</sub> catalyst gave a TOF of  $10,534 h^{-1}$ . Their TOF values reached a maximum point (almost the same



Fig. 5. FT-IR spectra of the (1) POL-PPh\_3 polymer and (2)  $2.0\,wt\%$  Rh/POL PPh\_3 catalyst.



**Fig. 6.** In situ FT-IR spectra of the 2.0 wt% Rh/POL-PPh<sub>3</sub> sample was treated with a premixed gas (C<sub>2</sub>H<sub>4</sub>:CO:H<sub>2</sub> = 1:1:1) at atmospheric pressure and 393 K for 60 min.

point), while the conversion of ethylene were 88.8% and 45.5%, respectively. Therefore the  $Rh/POL-PPh_3$  catalyst showed excellent activity and selectivity in the ethylene hydroformylation in fixed-bed reactor.

The long-term stability of the 0.125 wt% Rh/POL–PPh<sub>3</sub> catalyst was tested for hydroformylation of ethylene (Fig. 1). The ethylene conversion rate hardly decreased at all after over 1000 h, clearly demonstrating that the catalyst was extremely stable. The Rh load-ings of the fresh and spent 0.125 wt% Rh/POL–PPh<sub>3</sub> catalysts after over 1000 h time on stream were 0.1204% and 0.1206%, respectively. Besides, the Rh species in the product solution were even undetectable (<0.01 ppm).

# 3.1.2. Hydroformylation of 1-dodecene

Hydroformylation of 1-dodecene was carried on as a liquidphase application to evaluate the catalytic activity of the Rh/POL–PPh<sub>3</sub> catalyst. The 1-dodecene conversion of 86.4% and tridecanal linear/branch (l/b) ratio of 6.4 were obtained with a 0.125 wt% Rh/POL–PPh<sub>3</sub> catalyst (Table 2). The 504 h time onstream performance showed no apparent drop in activity and selectivity, demonstrating the excellent catalyst stability. The high l/b ratio of aldehydes may originate from the shape-selectivity imposed by the 0.7–1.5 nm micropores present in the Rh/POL–PPh<sub>3</sub> catalyst [25].

Based on these experimental data we concluded that in addition to their excellent catalytic activity, the Rh/POL-PPh<sub>3</sub> catalysts were extremely durable for hydroformylation reactions. In order to elucidate the superior catalytic performance of the Rh/POL-PPh<sub>3</sub> catalyst, HAADF-STEM, EXAFS, <sup>31</sup>P MAS NMR and in situ FT-IR techniques were used to investigate the state of the metal species over

Table 2

The performance of 1-dodecene  $^a$  hydroformylation over the 0.125 wt% Rh/POL–PPh\_3 catalyst.  $^b$ 

Entry	Time on stream (h)	Conversion (%)	l/b ratio
1	144	88.6	6.6
2	192	88.0	6.7
3	240	87.9	6.4
4	288	86.7	6.4
5	336	87.1	6.7
6	384	86.9	6.3
7	456	86.8	6.4
8	504	86.6	6.6

<sup>a</sup> 1-dodecene contained 0.11 ppm sulphur.

<sup>b</sup> Reaction conditions: a trickle-bed reactor, P = 1.0 MPa (CO:H<sub>2</sub> = 1:1), T = 373 K, GHSV of CO/H<sub>2</sub> = 5000 h<sup>-1</sup> and LHSV of 1-dodecene = 2.35 h<sup>-1</sup>.



Scheme 1. Proposed mechanism for ethylene hydroformylation over the Rh/POL-PPh3 catalysts.

the Rh/POL–PPh $_3$  catalyst and the coordination structure of the Rh/POL–PPh $_3$  catalyst.

# 3.2. Characterization of catalysts

#### 3.2.1. HAADF-STEM analysis

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of a fresh 0.125 wt% Rh/POL-PPh<sub>3</sub> catalyst (Fig. 2a) clearly show the isolated individual Rh species (indicated by the arrows) uniformly dispersed within the porous structures of the POL-PPh<sub>3</sub> support. Fig. 2b, an aberrationcorrected HAADF image of the Rh/POL-PPh<sub>3</sub> catalyst after over 1000 h of time-on-stream of continuous hydroformylation reaction, revealed clearly that the Rh species still maintained their isolated single sites without any observable sintering or aggregation effect. The Rh-containing molecular species were uniformly distributed on the surface of POL–PPh<sub>3</sub> support either in the fresh or used catalysts. Since the porous POL-PPh<sub>3</sub> support possesses a hierarchical pore structure, most of the Rh molecular species can access the pore walls (internal surfaces) inside the POL-PPh<sub>3</sub> support, resulting in enhanced long-term stability [26,27]. The internal surface area of the porous POL-PPh<sub>3</sub> support is relatively high so it can provide uniformly distributed and isolated Rh species even if the Rh loading is high. Fig. 2c and d shows HAADF-STEM images of a spent 2.0 wt% Rh/POL-PPh3 catalyst, confirming that all the Rh species were still dispersed as single sites.

Table 3			
The curve-fitting analysis	of the	EXAFS	traces.

Sample	Shell	Ν	R(Å)	$\Delta \delta^2x10^3(\text{\AA}^2)$	$R$ factor x $10^2$
0.125 wt% Rh/POL-PPh3 (used)	Rh-C	1	1.67	7.64	0.82
	Rh-P	3	2.26	4.5	
2.0 wt% Rh/POL-PPh <sub>3</sub> (used)	Rh-C	1	1.70	7.1	0.37
	Rh-P	3	2.24	3.5	
2.0 wt% Rh/POL-PPh <sub>3</sub> (fresh)	Rh-C	1	1.70	1.6	0.32
	Rh-P	3	2.22	3.3	
HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	Rh-C	1	1.68	14.7	0.08
	Rh-P	3	2.28	4.7	

# 3.2.2. EXAFS analysis

Fig. 3 shows a representative EXAFS (extended X-ray absorption fine structure) spectrum of the 0.125 wt% Rh/POL–PPh<sub>3</sub> sample after more than 1000 h of hydroformylation reaction. Only Rh–P and Rh–C coordination bonds [28,29] are revealed and no Rh–Rh bonds [30] can be detected, implying that the Rh ions had formed strong bonds with the exposed phosphorous atoms in the frame of the POL–PPh<sub>3</sub> (hereafter referred to as P-frame) and that the Rh species were dispersed as single sites. The Rh K-edge  $k^3$ -weighted Fourier transformation spectra from EXAFS for the fresh and used 2.0 wt% Rh/POL-PPh<sub>3</sub> catalysts (Fig. 3) further indicate that there was no detectable change between the fresh and spent catalysts. These results corroborate with those obtained from the aberration-corrected HAADF-STEM data.

# 3.2.3. <sup>31</sup>P MAS NMR analysis

The solid-state <sup>31</sup>P MAS NMR is employed to provide direct evidence for the interaction between the Rh species and the support of POL-PPh<sub>3</sub>. As shown in Fig. 4, the resonance peak at -5.8 ppm is attributed to the free phosphine in 3V-PPh<sub>3</sub> [31]. Meanwhile, the resonance peak at 26.4 ppm represents the coordinated phosphine in Rh-P carbonyl complex, indicating the coordination of the Rh species with phosphine species in POL-PPh<sub>3</sub> [32]. The formation of Rh-P carbonyl complex makes a contribution to the catalytic performance of the catalyst, as assigned in the literature [31,32]. When the Rh/POL-PPh3 catalyst was treated with syngas and employed in hydroformylation reaction (after 504 h of time-on-stream), the peak at 26.4 ppm appears and increases, while the peak at -5.8 ppm decreases. That means more coordinated phosphine was formed from free phosphine in 3V-PPh<sub>3</sub>. The peak intensities at 26.4 ppm and -5.8 ppm, respectively, for both a spent Rh/POL-PPh<sub>3</sub> and a HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/POL-PPh<sub>3</sub> sample are almost the same.

### 3.2.4. In situ IR analysis

When the Rh species are incorporated into POL–PPh<sub>3</sub> (Fig. 5 reveals the in situ FT-IR spectrum of the Rh/POL–PPh<sub>3</sub> catalyst adsorbed with a premixing gas ( $C_2H_4$ :CO:H<sub>2</sub> = 1:1:1). Four peaks of the sample at 2054, 2002, 1992 and 1959 cm<sup>-1</sup> are assigned to HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> species [16,33]. The HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> compound exists as two trigonal-bipyramidal isomers in equilibrium (one contains two equatorial phosphine ligands; the other



**Scheme 2.** Schematic diagrams of Rh/POL–PPh<sub>3</sub> catalysts illustrating the proposed structures of the active single sites of the Rh/POL–PPh<sub>3</sub> catalyst: (a) Rh ion tightly bonded to three phosphorus atoms of the Rh/POL–PPh<sub>3</sub> support with the Rh ion at the apex of tetragonal and (b) with the Rh ion located on the same plane as the three phosphorus atoms.

contains an equatorial and an apical phosphine ligand). The peaks at 2054 and  $1992 \,\mathrm{cm}^{-1}$  are attributed to ee-HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> species, while the peaks at 2002 and  $1959 \,\mathrm{cm}^{-1}$  are attributed to ea-HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> species. One peak of the Rh/POL–PPh<sub>3</sub> catalyst at 2078 cm<sup>-1</sup> is due to HRh(CO)(P-frame)<sub>3</sub> species [34]. Another peak at 2002 cm<sup>-1</sup> due to HRh(CO)(P-frame)<sub>3</sub> species is overlapped with the peak at 2002 cm<sup>-1</sup> assigned to HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> species. In situ FT-IR spectrum showed that active species, such as HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> and HRh(CO)(P-frame)<sub>3</sub>, similar to the conventional HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, may have been formed in the Rh/POL–PPh<sub>3</sub> catalysts during the hydroformylation reaction.

# 3.2.5. Discussion

<sup>31</sup>P MAS NMR experiments revealed that the spent Rh/POL–PPh<sub>3</sub> catalyst after hydroformylation of ethylene showed similar spectrum as a HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/POL–PPh<sub>3</sub> sample. Strong vibration bands assigned to HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> and HRh(CO)(P-frame)<sub>3</sub> species were also observed when treating the fresh Rh/POL-PPh<sub>3</sub> catalyst with a premixing gas of C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> by in situ FT-IR technique. Both the <sup>31</sup>P MAS NMR and FT-IR data suggest that the formation of Ph–P on the surface of POL–PPh<sub>3</sub> support, and the reaction mechanism of olefin hydroformylation over the Rh/POL–PPh<sub>3</sub> catalysts (Scheme 1) is similar to that over the homogeneous HRh(CO)(P-frame)<sub>3</sub> and HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> might be transformed into each other in dynamic.

The fitted radial distribution functions of the EXAFS spectra (Fig. 3 and Table 3) indicate that the Rh-P bond length is in the range of 2.22–2.28 Å and that of the Rh-C bond is in the range of 1.67–1.70 Å. According to the results of the curve-fitting analysis of the EXAFS traces for the supported Rh catalysts (Table 3), the structure of the Rh/POL-PPh<sub>3</sub> catalyst consists of three exposed phosphorous atoms in the frame of POL-PPh<sub>3</sub> and the coordinating Rh ion. High P-frame/Rh molecular ratio provides a possibility of active species formation. Based on all the data discussed above, we propose two probable structures of the Rh/POL-PPh<sub>3</sub> catalyst. Both structures contain an Rh ion tightly bonded to three phosphorous-frame atoms of the support (Scheme 2). The possible structure of the Rh/POL-PPh3 catalyst is that one Rh ion and two phosphorous-frame atoms are in the same plane; meanwhile another phosphorous-frame atom is nearly perpendicular to this plane, or one Rh ion and one phosphorous-frame atom are in the same plane; meanwhile the other two phosphorous-frame atoms are nearly perpendicular to this plane. The other possible structure of the Rh/POL-PPh<sub>3</sub> catalyst is that one Rh ion and three phosphorous-frame atoms are in the same plane. The rigidity of the P-frame sites results in the distortion of the Rh—P bonds due to the bond length and orientation effect among three phosphorous-frame atoms and one Rh ion. Thus one of the three coordination bonds might break easily for CO inserting into HRh(CO)(P-frame)<sub>3</sub> species to form HRh(CO)<sub>2</sub>(P-frame)<sub>2</sub> active intermediates, which initiate olefin hydroformylation reaction [37].

Developing ultrastable heterogenized homogenous catalysts, which maintain their high activity and selectivity, is a long-standing challenge and of great interest. In this work, the Rh/POL-PPh<sub>3</sub> catalyst showed ultrastable catalytic performance in fixed-bed hydroformylation reactions. This superior activity and stability performance might be originated from the following two main features: firstly, all the Rh atoms were existed in single Rh sites as confirmed by HAADF-STEM and EXAFS results which might be accounted for the high TOF values of hydroformylation reaction. Secondly, strong interaction between the active Rh-containing molecular species and the highly porous POL-PPh<sub>3</sub> support, which has been discussed above, is beneficial to preventing the leaching and sintering of Rh species.

### 4. Conclusions

In summary, the Rh/POL–PPh<sub>3</sub> catalyst has been demonstrated as an ultrastable heterogenized homogenous catalyst with high catalytic activity for fixed-bed hydroformylation of ethylene and 1-dodecene. HAADF-STEM and EXAFS results indicated that the Rh species existed in single Rh sites. The catalyst's stability originates from the formation of strong coordination bonds between the Rh ion and the exposed phosphorous atoms of the highly porous POL–PPh<sub>3</sub> support. The Rh/POL–PPh<sub>3</sub> catalyst provided high activity and selectivity because it maintained the catalytic functionalities similar to the homogeneous HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> complex, as demonstrated both by <sup>31</sup>P MAS NMR and in situ IR experiments. The Rh/POL–PPh<sub>3</sub> catalysts described in this report may provide a new concept in developing ultrastable heterogenized homogenous catalysts with high activity and selectivity.

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### References

- [1] D.J. Cole-Hamilton, Science 299 (2003) 1702–1706.
- [2] Y. Zhang, S.N. Riduan, Chem. Soc. Rev. 41 (2012) 2083–2094.
- [3] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature 339 (1989) 454-455.
- [4] K.T. Wan, M.E. Davis, Nature 370 (1994) 449-450.
- [5] J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P.
- Wijkens, D.M. Grove, G. van Koten, Nature 372 (1994) 659–663. [6] T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas, Nature 378 (1995) 159–162.
- [7] H. Gao, R.J. Angelici, J. Am. Chem. Soc. 119 (1997) 6937–6938.
- [8] A.J. Sandee, L.A. van der Veen, J.N.H. Reek, P.C.J. Kamer, M. Lutz, A.L. Spek,
- P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 38 (1999) 3231–3235.
  H. Zhu, Y. Ding, H. Yin, L. Yan, J. Xiong, Y. Lu, H. Luo, L. Lin, Appl. Catal. A: Gen.
- 245 (2003) 111–117. [10] L. Yan, Y.J. Ding, H.J. Zhu, J.M. Xiong, T. Wang, Z.D. Pan, L.W. Lin, J. Mol. Catal.
- A: Chem. 234 (2005) 1–7. [11] R. Abu-Reziq, H. Alper, D. Wang, M.L. Post, J. Am. Chem. Soc. 128 (2006)
- [11] K. ADU-REZIQ, H. AIPEL, D. Wang, M.L. POSL, J. AM. CHEM. Soc. 128 (2006) 5279–5282.
   [21] S. W. Ding, L. Gu, Q. Wang, Y. Zhang, W. C. Gung, G. Y. Gu, W. Wang, J. A.
- [12] S.-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.-Y. Su, W. Wang, J. Am. Chem. Soc. 133 (2011) 19816–19822.
- [13] N. Sudheesh, S.K. Sharma, R.S. Shukla, R.V. Jasra, J. Mol. Catal. A: Chem. 316 (2010) 23–29.
- [14] Z. Nairoukh, J. Blum, J. Mol. Catal. A: Chem. 358 (2012) 129-133.
- [15] S.K. Sharma, P.A. Parikh, R.V. Jasra, J. Mol. Catal. A: Chem. 316 (2010) 153-162.

- [16] L. Yan, Y.J. Ding, L.W. Lin, H.J. Zhu, H.M. Yin, X.M. Li, Y. Lu, J. Mol. Catal. A: Chem. 300 (2009) 116-120.
- [17] X. Li, Y. Ding, G. Jiao, J. Li, R. Lin, L. Gong, L. Yan, H. Zhu, Appl. Catal. A: Gen. 353 (2009) 266-270.
- [18] F. Marras, A.M. Kluwer, J.R. Siekierzycka, A. Vozza, A.M. Brouwer, J.N.H. Reek, Angew. Chem. Int. Ed. 49 (2010) 5480-5484.
- [19] F. Marras, J. Wang, M.-O. Coppens, J.N.H. Reek, Chem. Commun. 46 (2010) 6587-6589.
- [20] R. Franke, D. Selent, A. Börner, Chem. Rev. 112 (2012) 5675-5732.
- [21] M.J. Climent, A. Corma, S. Iborra, Chem. Rev. 111 (2010) 1072-1133. [22] D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, Chem. Rev. 112 (2012)
- 3959-4015. [23] P. Kaur, J.T. Hupp, S.T. Nguyen, ACS Catal. 1 (2011) 819-835.
- [24] M. Rose, ChemCatChem 6 (2014) 1166–1182.
- [25] Q. Sun, M. Jiang, Z. Shen, Y. Jin, S. Pan, L. Wang, X. Meng, W. Chen, Y. Ding, J. Li, F.-S. Xiao, Chem. Commun. 50 (2014) 11844-11847.
- [26] D.S. Shephard, W. Zhou, T. Maschmeyer, J.M. Matters, C.L. Roper, S. Parsons, B.F.G. Johnson, M.J. Duer, Angew. Chem. Int. Ed. 37 (1998) 2719-2723.

- [27] P. Li, S. Kawi, J. Catal. 257 (2008) 23-31.
- [28] S.G. Fiddy, J. Evans, T. Neisius, X.-Z. Sun, Z. Jie, M.W. George, Chem. Commun. (2004) 676-677.
- [29] J.-R. Chang, H.-M. Lin, S.-W. Cheng, C.-K. Tseng, D.-L. Tzou, S.-G. Shyu, J. Mol. Catal. A: Chem. 329 (2010) 27-35.
- [30] C. Bianchini, D.G. Burnaby, J. Evans, P. Frediani, A. Meli, W. Oberhauser, R. Psaro, L. Sordelli, F. Vizza, J. Am. Chem. Soc. 121 (1999) 5961-5971.
- [31] X. Lan, W. Zhang, L. Yan, Y. Ding, X. Han, L. Lin, X. Bao, J. Phys. Chem. C 113 (2009) 6589-6595.
- [32] K. Mukhopadhyay, A.B. Mandale, R.V. Chaudhari, Chem. Mater. 15 (2003) 1766–1777.
- [33] E.B. Walczuk, P.C.J. Kamer, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. 42 (2003) 4665-4669.
- [34] L.A. Gerritsen, A. Van Meerkerk, M.H. Vreugdenhil, J.J.F. Scholten, J. Mol. Catal. 9 (1980) 139-155.
- [35] D. Evans, J.A. Osborn, G. Wilkinson, J. Chem. Soc. A (1968) 3133-3142.
- [36] C.K. Brown, G. Wilkinson, J. Chem. Soc. A (1970) 2753-2764.
- [37] S.C. van der Slot, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.A. Iggo, B.T. Heaton, Organometallics 20 (2001) 430-441.