

# Ligand modified real heterogeneous catalysts for fixed-bed hydroformylation of propylene

Li Yan<sup>a,c</sup>, Yun J. Ding<sup>a,b,\*</sup>, He J. Zhu<sup>a</sup>, Jian M. Xiong<sup>a</sup>,  
Tao Wang<sup>a</sup>, Zhen D. Pan<sup>a</sup>, Li W. Lin<sup>b</sup>

<sup>a</sup> Natural Gas Utilization and Applied Catalysis Laboratory, Dalian Institute of Chemical Physics,  
Chinese Academy of Sciences, 457 Zhongshan Rd., Dalian 116023, China

<sup>b</sup> The State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
457 Zhongshan Rd., Dalian 116023, China

<sup>c</sup> Graduate School of Chinese Academy of Sciences, Beijing, China

Received 15 September 2004; received in revised form 27 January 2005; accepted 28 January 2005  
Available online 20 March 2005

## Abstract

A novel ligand modified heterogeneous catalyst has been developed for hydroformylation of propylene, which showed excellent activity, selectivity and stability and need not be separated from the product after reaction in a fixed-bed reactor. The coordination bonds between triphenyl phosphine (PPh<sub>3</sub>) and Rh/SiO<sub>2</sub> were confirmed by means of thermogravimetric (TG), solid-state <sup>31</sup>P NMR, XPS and FT-IR. Two types of active species for hydroformylation were formed, which were proved by in situ FT-IR techniques. The problem of metal leaching was greatly reduced by directly fastening Rh particles on the support, and the active Rh species that was responsible for the outstanding performance of propylene hydroformylation was tightly bound by the very strong metal–metal bonds. No sign of deactivation was observed over a period of more than 1000 h on the condition that PPh<sub>3</sub> was added at 300–350 h of time on stream.

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**Keywords:** Hydroformylation; Propylene; Heterogeneous; Rh/SiO<sub>2</sub>; Phosphine ligands

## 1. Introduction

Hydroformylation is one of the largest industrial processes (millions of tonnes annually) catalyzed by homogeneous transition metal complexes [1,2]. In spite of the high level of implemented commercial processes, their practical applications have been limited by difficulties in achieving industrially viable catalyst–product separation [3]. A series of studies of this catalyst system led to an understanding of the factors that govern reactivity and selectivity [4]:  $\sigma$ -donor ligands may inhibit the reaction completely, switching to stronger  $\pi$ -acceptor ligands such as phosphites leading to more active and more selective hydroformylation catalysts [5–8].

The new hydroformylation processes under investigation can be broadly grouped into two types. One is often referred to anchored catalysts [9], tethered catalysts [10], supported aqueous phase (SAP) catalysts [11,12] and supported ionic liquid phase (SILP) catalysts [13,14] as heterogenized homogeneous catalysts; the other is the biphasic system [15] using aqueous biphasic [16], supercritical fluids [17–19] and ionic liquids [20]. In these works, interesting concepts have emerged, however, they suffer from low selectivity, reactivity (TOF) and recyclability, high metal leaching, or expensive ligands, and hence, need to be improved for practical applications [21].

Although hydroformylation of alkenes by heterogeneous catalysts is less extensively studied [22–24] than that by homogeneous transition metal complexes [25,26], heterogeneous hydroformylation is a promising process from academic and practical points of view. Therefore, we proposed

\* Corresponding author. Tel.: +86 411 84379143; fax: +86 411 84379143.  
E-mail address: [dyl@dicap.ac.cn](mailto:dyl@dicap.ac.cn) (Y.J. Ding).

to modify Rh/SiO<sub>2</sub> with triphenyl phosphine (PPh<sub>3</sub>), in the hope that there might be chemical adsorption of PPh<sub>3</sub> on Rh/SiO<sub>2</sub>, which may promote the in situ growth of the active species for hydroformylation in syngas atmosphere, and that the problem of metal leaching might be resolved by directly fastening the metal particles on the support. This catalyst designated by PPh<sub>3</sub>-Rh/SiO<sub>2</sub> was applied to the hydroformylation of propylene.

## 2. Experimental

### 2.1. Synthesis of PPh<sub>3</sub>-Rh/SiO<sub>2</sub> catalyst

The catalyst was prepared using a commercial SiO<sub>2</sub> (Qingdao Haiyang Chemicals Plant, specific surface area 250 m<sup>2</sup> g<sup>-1</sup>) as support. The support was impregnated with an aqueous solution of rhodium chloride (Johnson Matthey) using the incipient wetness method. After impregnation, the samples were first dried at 373 K, then calcined at 673 K in a quartz tube and finally reduced by H<sub>2</sub> at 673 K. The Rh loading was 1 wt%. Rh/SiO<sub>2</sub> precursor was introduced into the PPh<sub>3</sub> solution in tetrahydrofuran and this mixture was stirred for 0.5 h. The solvent was removed under vacuum at room temperature, and the resulting black PPh<sub>3</sub>-Rh/SiO<sub>2</sub> (the molar ratio of P:Rh = 10:1, unless specified) was stored under argon atmosphere. When the activity and the selectivity tended to decline in the range of about 300–350 h time on stream, the PPh<sub>3</sub>-Rh/SiO<sub>2</sub> catalyst was taken out from the reactor and allowed to contact the PPh<sub>3</sub> solution in tetrahydrofuran. The solvent was removed under vacuum at room temperature after this mixture was stirred for 0.5 h. Thus, treated PPh<sub>3</sub>-Rh/SiO<sub>2</sub> catalyst was employed in the experiments of 1000 h stability test of the catalyst. HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was prepared according to a procedure reported earlier [27], and dissolved with PPh<sub>3</sub> (the total molar P:Rh ratio = 10:1) in toluene. Then SiO<sub>2</sub> was introduced into this solution and the mixture was stirred for 0.5 h. Finally the yellow HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub> was obtained after removing toluene. All manipulations were carried out under an argon atmosphere, and all reagents were dehydrated with CaH<sub>2</sub> and degassed with argon.

### 2.2. Hydroformylation reaction

The hydroformylation was conducted in a continuous flow fixed-bed reactor (i.d. 4.6 mm). The effluent was passed through a condenser filled with 100 ml of cold de-ionized water. Butyraldehyde in the products of hydroformylation was captured completely by dissolution into the water in the condenser. An HP-6890N GC with an FFAP column, using an FID detector and ethanol as an internal standard, analyzed the aqueous solution containing butyraldehyde. The tail gas was analyzed on-line on an HP-6890N GC with a Porapak-QS column and a TCD detector.

### 2.3. Instrumentation

Solid-state <sup>31</sup>P-MAS NMR experiments were performed on a Bruker DRX-400 spectrometer. Data were obtained by measuring the samples using a frequency of 161.97 MHz, a pulse width of  $\pi/8$ , a delay of 2.0 s, and 100 scans. Solid-state <sup>31</sup>P NMR chemical shifts were reported relative to 85% H<sub>3</sub>PO<sub>4</sub>. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Leybold AG LHS-12 MAS instrument, using radiation of unmonochromatized Mg K $\alpha$  (photo energy –1253.6 eV). In situ FT-IR spectra were measured by a Bruker EQUINOX 55 single-beam Fourier Transform infrared spectrometer equipped with a DTGS detector. All spectra were recorded with 16 scans with a resolution of 4 cm<sup>-1</sup>. The sample wafer was mounted in a high temperature/high pressure cell (SPECAC INC P/N 5850) fitted with ZnSe windows and an automatic temperature controller; the cell is a water-cooled, stainless steel chamber. The sample was reduced in flowing H<sub>2</sub> at 393 K for 1 h. After reduction, the catalyst was cooled down to 323 K in a flow of N<sub>2</sub> and was subjected to FT-IR measurement (spectrum A). Subsequently, a premixed (H<sub>2</sub>:CO:C<sub>2</sub>H<sub>4</sub> = 1:1:1) gas was introduced into this system, and kept flowing for 30 min under atmospheric pressure. After purging the chamber with high-purity nitrogen for 30 min, spectrum B was recorded. Subtracting spectrum A from spectrum B gave a final FT-IR spectrum. We also analyzed the aqueous solution containing butyraldehyde with an inductive coupled plasma-atomic emission spectroscopy (ICP-AES) measurement to detect metal leaching. PPh<sub>3</sub> in the aqueous solution were analyzed by an Agilent 5973N GC–MS instrument.

## 3. Results and discussion

In order to obtain information about the influence of PPh<sub>3</sub> on the Rh/SiO<sub>2</sub> catalyst, we have made a comparison of the catalytic performance of the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>-derived catalyst (HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub>), conventional heterogeneous catalyst (Rh/SiO<sub>2</sub>) and PPh<sub>3</sub>-Rh/SiO<sub>2</sub> with the same concentration of Rh in a fixed-bed reactor under the same conditions (Table 1). It is obvious that PPh<sub>3</sub>-Rh/SiO<sub>2</sub> showed far higher activity (TOF, mol-butyr-aldehyde/(mol-Rh h)) and conversion of propylene) than that of the conventional heterogeneous catalyst. However, the activity was lower than

Table 1  
Comparison of the catalytic performance among HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub>, Rh/SiO<sub>2</sub> and PPh<sub>3</sub>-Rh/SiO<sub>2</sub> catalysts

| Catalyst  | Conversion (%) | TOF (mol-butyr-aldehyde/(mol-Rh h)) | n/i ratio |
|---|----------------|-------------------------------------|-----------|
| HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub> /SiO <sub>2</sub> | 39.9           | 230                                 | 8.8       |
| Rh/SiO <sub>2</sub>                                       | 0.12           | 1.2                                 | 3.1       |
| PPh <sub>3</sub> -Rh/SiO <sub>2</sub>                     | 27.1           | 131                                 | 8.6       |

Reaction conditions:  $T = 393$  K; time on stream = 4 h;  $P = 1.0$  MPa;  $SV = 2000$  h<sup>-1</sup>.

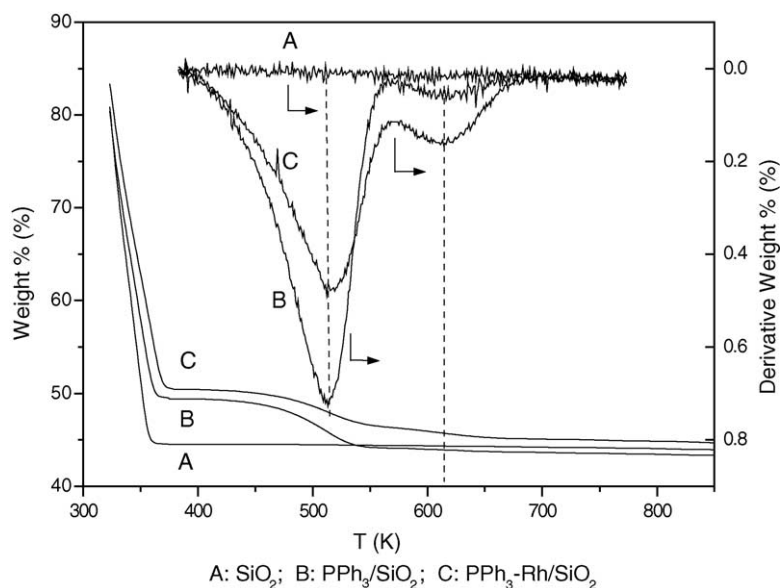


Fig. 1. Thermogravimetric analysis (TG) and TG derivative profiles of  $\text{SiO}_2$ ,  $\text{PPh}_3/\text{SiO}_2$  and  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  samples.

the  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ -derived catalyst due to the exposure of 67% of Rh particles, while the  $n/i$  ratio for  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  was comparable to that for the  $\text{HRh}(\text{CO})(\text{PPh}_3)_3/\text{SiO}_2$ . After the reaction, the solution was transparent and colorless.

The similar performance of  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  and  $\text{HRh}(\text{CO})(\text{PPh}_3)_3/\text{SiO}_2$  for hydroformylation of propylene, including propylene conversion, selectivity and  $n/i$  ratio of butyraldehydes, allowed us to propose that there might be coordination bonds between the ligands and the highly dispersed Rh species on the surface of Rh nano-particles. Consequently, we made an investigation of the interaction between  $\text{PPh}_3$  and  $\text{Rh}/\text{SiO}_2$  by means of thermogravimetric (TG), solid-state  $^{31}\text{P}$  NMR, XPS and in situ FT-IR techniques.

Thermogravimetric analysis and TG derivative profiles of the  $\text{SiO}_2$ ,  $\text{PPh}_3/\text{SiO}_2$  and  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  samples are demonstrated in Fig. 1. The great weight loss before 383 K is due to the solvent evaporation. A large peak at about 513 K and a relatively small peak at about 613 K are assigned to the removal of physically and chemically adsorbed  $\text{PPh}_3$ , respectively. Compared to  $\text{PPh}_3/\text{SiO}_2$ ,  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  shows a decrease in physically adsorbed  $\text{PPh}_3$  and an increase in chemically adsorbed  $\text{PPh}_3$ .

Solid-state  $^{31}\text{P}$  NMR techniques can provide evidence for the formation of the coordination bond. Solid-state  $^{31}\text{P}$  NMR spectra of  $\text{PPh}_3$  modified  $\text{Rh}/\text{SiO}_2$  catalysts are shown in Fig. 2. In the spectrum A, there is a sharp absorption peak at  $-5.7$  ppm assigned to the free  $\text{PPh}_3$  in the  $\text{PPh}_3/\text{SiO}_2$  sample. A broad peak at  $+35.4$  ppm due to the phosphines of rhodium complex appears in the spectrum of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3/\text{SiO}_2$  sample (Fig. 2 Curve D) [28]. As both the chemical shift and the feature of the absorption at  $+30.1$  ppm in spectrum B are similar to those of the peak at  $+35.4$  ppm in spectrum D, it is assigned to  $\text{PPh}_3$  that chemically adsorbed on the surface of

Rh nano-particles. The chemical shift difference reasonably interpreted by assuming that the electronic state around these Rh species have been changed after being coordinated by  $\text{PPh}_3$ , and is different from that around  $\text{Rh}^{+1}$ . The sharp peak at  $-5.6$  ppm in  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  sample is attributed to the free  $\text{PPh}_3$ . Only a slight increase in the free  $\text{PPh}_3$  was observed after the  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$  catalyst was treated by syngas.

The XPS results imply that  $\text{Rh}^{\delta+}$  ( $0 < \delta < 1$ ) species with the binding energy of 307.5–308.0 eV appears on the surface of supported metal nano-particles after  $\text{PPh}_3\text{-Rh}/\text{SiO}_2$

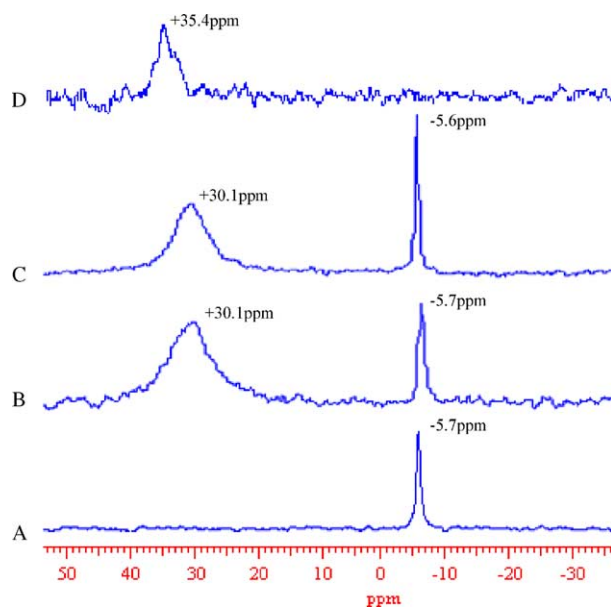


Fig. 2. Solid-state  $^{31}\text{P}$  NMR spectra of  $\text{PPh}_3$  modified  $\text{Rh}/\text{SiO}_2$  catalysts (the molar ratio of P:Rh = 3:1): (A)  $\text{PPh}_3/\text{SiO}_2$ ; (B)  $\text{PPh}_3\text{-1%Rh}/\text{SiO}_2$ ; (C)  $\text{PPh}_3\text{-1%Rh}/\text{SiO}_2$  treated by syngas; (D)  $\text{HRh}(\text{CO})(\text{PPh}_3)_3/\text{SiO}_2$ .

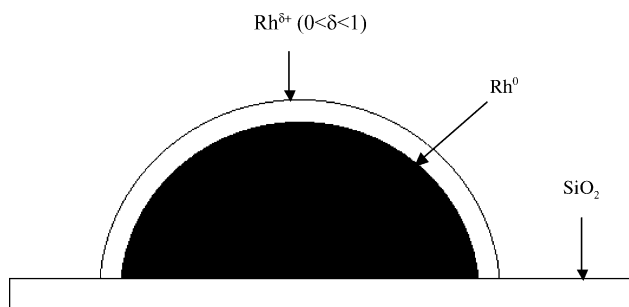


Fig. 3. Possible distributions of Rh species in PPh<sub>3</sub>-Rh/SiO<sub>2</sub> catalysts.

sample was treated with syngas, while only Rh<sup>0</sup> (307.2 eV) species was detected in Rh/SiO<sub>2</sub>, Rh/SiO<sub>2</sub> (treated by syngas) and PPh<sub>3</sub>-Rh/SiO<sub>2</sub> samples. These binding energies are found to be in agreement with the literature values [29,30]. It is to be noted that Rh<sup>δ+</sup> (0 < δ < 1) species in situ formed after the PPh<sub>3</sub>-Rh/SiO<sub>2</sub> sample was treated with syngas; most Rh<sup>0</sup> species in the Rh nano-particle on SiO<sub>2</sub> could be oxidized to Rh<sup>δ+</sup> as a result of reaction with syngas. We presume distribution of Rh species as shown in Fig. 3, the Rh particle was directly fastened to SiO<sub>2</sub> by interaction of Rh and SiO<sub>2</sub> (Rh–O bonds) after calcination and most Rh species at the outer layer of Rh nano-particle were reduced to Rh<sup>0</sup> species. After they had been chemically adsorbed by PPh<sub>3</sub>, these Rh<sup>0</sup> species at the surface were oxidized to Rh<sup>δ+</sup> (0 < δ < 1) species by syngas and bound to the Rh<sup>0</sup> layer in the bulk of metallic nanoparticles, and all these exterior Rh species were tightly bound by the very strong metal–metal bonds [31]. When the coordination bonds between Rh<sup>δ+</sup> and ligands are broken during catalytic reactions, Rh species is fixed on SiO<sub>2</sub> by the Rh–O bonds and the very strong metal–metal bonds and PPh<sub>3</sub> is inevitably leached in the case of PPh<sub>3</sub>-Rh/SiO<sub>2</sub>, however, the Rh ion may break away from the support in a homogeneous catalyst heterogenized on a solid support [21]. The Rh–O bonds and the strong metal–metal bonds is the reason for the problem of metal leaching being greatly reduced.

Fourier transform infrared transmittance spectra of Rh/SiO<sub>2</sub>, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub> and PPh<sub>3</sub>-Rh/SiO<sub>2</sub> are demonstrated in Fig. 4. There are three primary carbonyl species in the FT-IR spectrum of Rh/SiO<sub>2</sub>: geminal dicarbonyl of Rh(CO)<sub>2</sub> with asymmetric and symmetric bands at 2095 and 2031 cm<sup>-1</sup>; linear Rh<sub>x</sub>-CO at 2066 cm<sup>-1</sup>; and bridged Rh<sub>2</sub>-CO at 1867 cm<sup>-1</sup>, as originally assigned by Yang and Garland [32]. According to the earlier report of Wilkinson and co-workers [27,33], the broad band at 2005–2035 cm<sup>-1</sup> in the spectrum of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub> suggests the existence of three species: HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, 2005 cm<sup>-1</sup>; [Rh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, 2017 cm<sup>-1</sup> and HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 2035 cm<sup>-1</sup>, revealing the following equilibria:

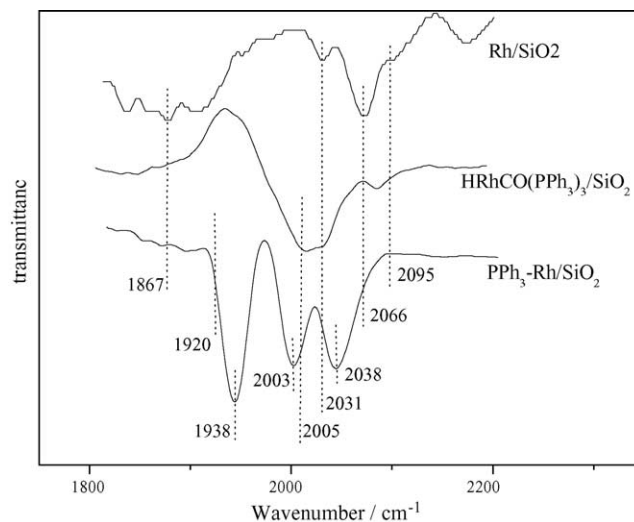
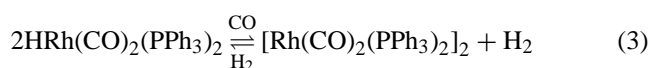


Fig. 4. Infrared (Fourier transform) transmittance spectra of Rh/SiO<sub>2</sub>, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub> and PPh<sub>3</sub>-Rh/SiO<sub>2</sub> treated by premixed.



They also pointed out that in the above equilibria, the active species for hydroformylation was HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, while the most stable species was [Rh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sub>2</sub>. The HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> species and HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> species predominate on PPh<sub>3</sub>-Rh/SiO<sub>2</sub> as revealed by the peaks at 1920, 2003 cm<sup>-1</sup> and 1938, 2038 cm<sup>-1</sup>, respectively. Therefore, it is reasonable to consider that the active species of HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> for hydroformylation in situ form on the surface of Rh/SiO<sub>2</sub> catalysts after PPh<sub>3</sub>-Rh/SiO<sub>2</sub> is treated with a premixed gas (H<sub>2</sub>:CO:C<sub>2</sub>H<sub>4</sub> = 1:1:1).

On the basis of TG, solid-state <sup>31</sup>P NMR, XPS and in situ FT-IR results, we could conclude that chemical interactions do exist between PPh<sub>3</sub> and Rh/SiO<sub>2</sub>, and the chemically adsorbed PPh<sub>3</sub> promotes the in situ formation of HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, which is responsible for active and selective hydroformylation of olefins, while the Rh–O bonds and the strong metal–metal bonds of Rh species might prevent Rh from leaching. The Bruker software WINNMR was employed for deconvolution using Gaussian–Lorentzian line-shapes. By integration of Curve B in Fig. 2, we found the percent area of the peak at +30.1 ppm was 77%; therefore, the molar ratio of coordinated PPh<sub>3</sub> to exposed Rh particles was calculated as follows:

$$\frac{\text{coordinated PPh}_3}{\text{exposed Rh particles}} = \frac{\text{the molar ratio of PPh}_3}{\text{Rh}} \times \frac{\text{the percent area of coordinated PPh}_3}{\text{the exposure of Rh}}$$

where the exposure of Rh is 67% based on 0.64 ml/g STP H<sub>2</sub> adsorbed on Rh/SiO<sub>2</sub> in hydrogen chemisorption experiment.

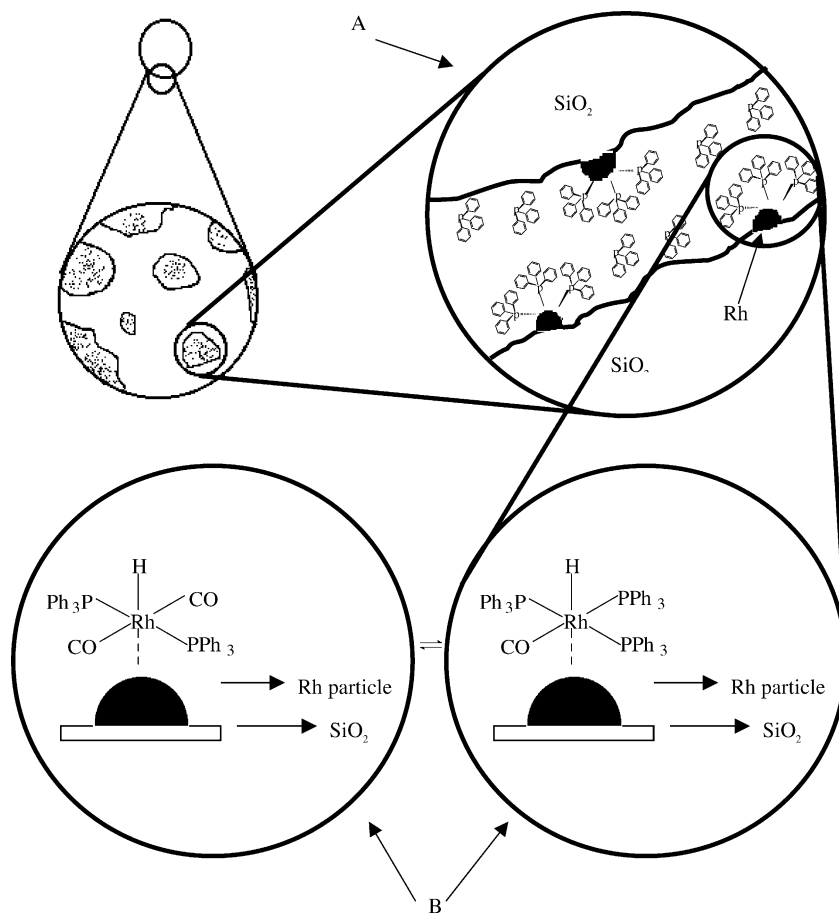


Fig. 5. (A) Model of  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst and (B) two possible models of  $\text{PPh}_3\text{-Rh/SiO}_2$  treated with syngas.

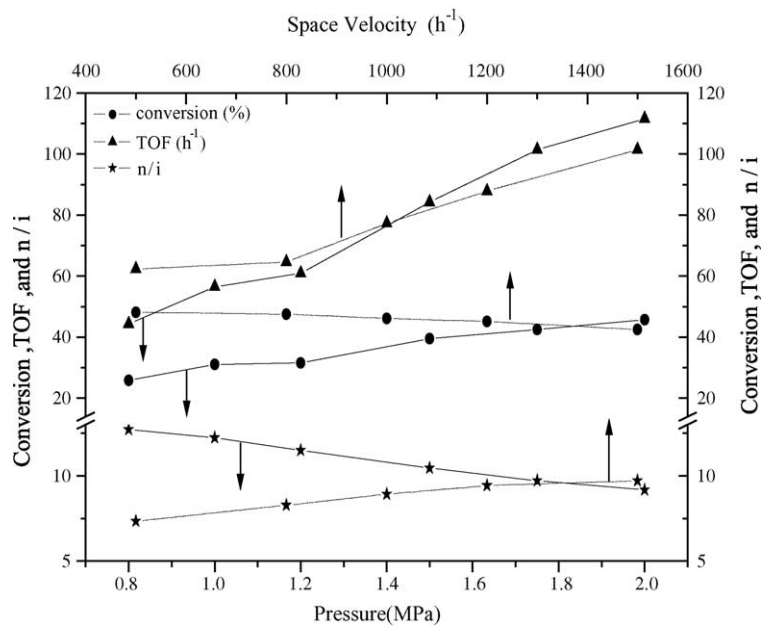


Fig. 6. Influence of space velocity ( $P = 1.75 \text{ MPa}$ ,  $T = 393 \text{ K}$ ) and pressure ( $\text{SV} = 1500 \text{ h}^{-1}$ ,  $T = 393 \text{ K}$ ) on the activity of hydroformylation of propylene over  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst.



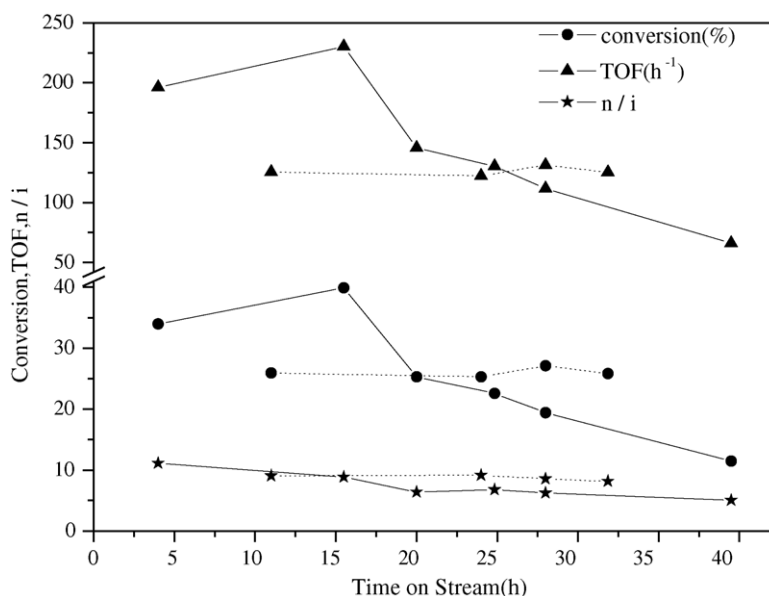


Fig. 7. Stability of hydroformylation of propylene over  $\text{HRh(CO)(PPh}_3)_3/\text{SiO}_2$  (the solid line) catalyst and  $\text{PPh}_3\text{-Rh/SiO}_2$  (the dot line) catalyst. Reaction conditions:  $P = 1.0 \text{ MPa}$ ,  $\text{SV} = 2000 \text{ h}^{-1}$ ,  $T = 393 \text{ K}$ .

The molar ratio of coordinated  $\text{PPh}_3$  to exposed Rh particles was about 3. Accordingly, we have made a model of our catalyst in Fig. 5 to expound the  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst clearly.

With the purpose of investigating the application of the  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst, a series of propylene hydroformylation reactions was carried out in a fixed-bed reactor under different conditions. Fig. 6 shows the effect of space velocity and pressure on the activity of  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst. The turnover frequency of formation of butyraldehyde and its  $n/i$  ratio increase with the space velocity, while the conversion of propylene decreases slightly. It is found that the TOF and conversion of propylene increase and the  $n/i$  ratio decreases with pressure. Due to the low reaction temperature of hydroformylation and the coordination bonds between Rh nano-particles and  $\text{PPh}_3$ , the selectivity of butyraldehyde under all process conditions is as high as over 99.5% as expected.

The evidence obtained from ICP-AES measurements shows that no Rh species in excess of 0.01 ppm level was detected in the product solutions, while  $\text{PPh}_3$  was found in the GC-MS analysis of the product solutions. To make a comparison between  $\text{HRh(CO)(PPh}_3)_3/\text{SiO}_2$  and  $\text{PPh}_3\text{-Rh/SiO}_2$ , we also tested their stabilities and the results are given in Fig. 7. It is obvious that the activity and the  $n/i$  ratio of  $\text{HRh(CO)(PPh}_3)_3/\text{SiO}_2$  reduce quickly after a run of 16 h, while those of  $\text{PPh}_3\text{-Rh/SiO}_2$  remain unchanged after a run of 33 h. In particular, we have carried out the hydroformylation of propylene in a fixed-bed reactor for a period of over 1000 h with the propylene conversion,  $n/i$  ratio and TOF remain approximately the same, on the condition that  $\text{PPh}_3$  is supplemented at about 300–350 h of time on stream, and some representative data are shown in Table 2. Consequently,

Table 2

Stability of hydroformylation of propylene over the hybrid  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst ( $P = 1.0 \text{ MPa}$ ,  $\text{SV} = 1359 \text{ h}^{-1}$ ,  $T = 373 \text{ K}$ )

| Time on stream (h) | Conversion (%) | TOF (mol butyraldehyde/mol Rh h) | $n/i$ ratio |
|--------------------|----------------|----------------------------------|-------------|
| 186                | 17.9           | 89.0                             | 11.5        |
| 516                | 16.6           | 81.9                             | 10.1        |
| 813                | 17.0           | 86.2                             | 9.97        |
| 994                | 15.4           | 72.6                             | 9.69        |

we could deduce a conclusion that  $\text{PPh}_3\text{-Rh/SiO}_2$  catalyst is nearly free of Rh metal leaching in the hydroformylation of propylene.

#### 4. Conclusion

The present work has shown that  $\text{PPh}_3\text{-Rh/SiO}_2$  is a novel heterogeneous catalyst for hydroformylation of propylene. The TG, solid-state  $^{31}\text{P}$  NMR, XPS and in situ FT-IR techniques all confirm that  $\text{PPh}_3$  molecules could be chemically adsorbed on the heterogeneous  $\text{Rh/SiO}_2$ , and that they promote the in situ formation of  $\text{HRh(CO)(PPh}_3)_3$  species and  $\text{HRh(CO)}_2(\text{PPh}_3)_2$  species, which play an important role in improving the activity and selectivity of olefin hydroformylation. The problem of metal leaching is greatly reduced by directly fastening Rh nano-particles to the support, and Rh species are tightly bound by the Rh–O bonds and the very strong metal–metal bonds. Our observations are limited to the effect of  $\text{PPh}_3$  on  $\text{Rh/SiO}_2$ , and further investigation on different ligands and supports would disclose an interesting prospective in heterogeneous catalysis.

## Acknowledgments

This work is supported financially by the National Natural Science Foundation of China (20073046) and Chinese Science and Technology Ministry (Grant no. G2003CB615803). We thank Ms. X.M. Liu, Prof. X.W. Han and Dr. H. Lei for the measurement of solid-state  $^{31}\text{P}$  NMR and XPS, respectively.

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