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The PPh_3 ligand modified Rh/SiO_2 catalyst for hydroformylation of olefins

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Abstract

A novel family of hybrid catalyst with high turnover frequency (TOF) and high selectivity towards aldehydes for hydroformylation of olefins could be successfully approached through direct coordination with the PPh_3 ligand to the highly dispersed Rh metal particle precursors. A further advantage is that the catalyst is easily prepared and recyclable. The results revealed that hydroformylation of olefins to aldehydes dominantly took place on the surface of PPh_3 ligand modified Rh metal particles of the hybrid catalyst. It was found that the formation of chemical coordination bond between the Rh metal particles and the lone-pair electron of PPh_3 was evident through the TG and ^{31}P NMR measurement. Moreover, the addition of PPh_3 onto the Rh/SiO_2 exert a significant influence on the adsorption state of reactant CO, H_2 and C_2H_4 on the PPh_3–Rh/SiO_2 sample, which probably lead to good catalytic performances for hydroformylation of olefins.

Keywords: Hydroformylation; Silica supported Rh metal; Hybrid catalyst; PPh_3 ligand

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1. Introduction

The heterogeneous Rh/SiO_2 catalyst for hydroformylation of olefins has the advantage of easy separation of catalysts from the products but has the disadvantages of low activity and selectivity. The catalytic performances in heterogeneous catalysis are generally improved by addition of various promoters, such as, Zn, Se, Na, etc. [1–5]. However, the activities and selectivity of the heterogeneous Rh–Zn/SiO_2, Rh–Ag/SiO_2 catalyst are still much lower.

The homogeneous rhodium phosphine complexes, such as conventional $HRh(CO)(PPh_3)_3$ (where PPh_3 is triphenylphosphine) complex, are good hydroformylation catalysts with high activity and high selectivity under mild conditions [6]. However, homogeneous catalysts are difficult to be recovered from products [7,8]. Approaches for immobilization of homogeneous complex to solve this problem have been explored, which can broadly be grouped into two types. Firstly, biphasic systems involve in designing the catalyst so that it is soluble in a solvent as a “liquid carrier”, under some conditions, is immiscible with the reaction products [9–13]. Another strategy has long been attachment of the catalyst to polymers resin or silica and the separation are recyclable by a simple filtration [14–17]. Although these heterogenized homogeneous catalysts have been well developed, until now, only water–oil biphasic catalysis system has been successfully employed in the hydroformylation of propylene.

In this paper, a new type of hybrid PPh_3 modified Rh/SiO_2 (PPh_3–Rh/SiO_2) catalyst for hydroformylation of olefins with high activity and high selectivity towards aldehydes were developed. Our support of catalyst and the methods for preparation of PPh_3–Rh/SiO_2 catalyst differed from those of all previously reported in literature. Moreover, we make an attempt to clarify the catalytic active sites of the hybrid phosphine-modified Rh/SiO_2 catalyst in our work.

2. Experimental

2.1. Catalyst preparation

Heterogeneous Rh/SiO_2 catalyst was prepared by incipient wetness impregnation of silica (ca. 100 mesh) with a

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solution of $RhCl_3$. The Rh loading of Rh/SiO_2 was 1 wt.%. The impregnated sample was dried first at room temperature, then at 393 K, and subsequently calcined at 573 K for 3 h, and finally reduced in a flow of H_2 at 573 K for 3 h. The reduced black sample was further washed with boiling deionized water to deionize the Cl^{-1} ion on the Rh/SiO_2. Then the obtained sample was reduced again to remove oxygen and water.

All preparations of hybrid PPh_3–Rh/SiO_2 catalyst was performed using standard Schlenk techniques under an argon atmosphere, and all reagents were dehydrated by CaH_2 and degassed with argon. Phosphine was firstly added to cyclohexane solvent (the volume of cyclohexane was 1.5 times of that of Rh/SiO_2 catalyst) and stirred until it dissolved completely. Rh/SiO_2 (the molar ratio of P:Rh = 15:1, unless specified) precursor was introduced to this solution, then the obtained slurry was stirred for 1 h. and lastly the solvent was evacuated under vacuum at room temperature for 1 h. The final product was stored under argon at room temperature.

2.2. Catalyst evaluation

When conducting the hydroformylation reaction in a slurry-bed reactor, 60 ml cyclohexane and 15 ml olefins were added to a 300 ml stainless-steel stirred vessel, and then the hybrid PPh_3–Rh/SiO_2 catalyst was carefully introduced into the reactor under Ar atmosphere. Then the reactor was purged three times with a mixture of CO/H_2 ($H_2/CO = 1{:}1$, 1.0 MPa), adjusted the reaction pressure to 1.0 MPa, and heated to the reaction temperature of 373 K. The products of hydroformylation were analyzed by a Varian 3800 gas chromatograph with a SE-30 capillary column.

2.3. Catalyst characterization

Thermogravimetric analysis (TG) of the hybrid catalyst was carried out under argon atmosphere on a PerkinElmer Pyris 1 TGA thermogravimetric analyzer. CP-MAS ^{31}P NMR measurements were recorded on a Bruker DRX-400 spectrometer at 60.7 MHz at the State MMR Center. Phosphorus-31 NMR chemical shifts were reported relative to 85% H_3PO_4. The heptanes had been soaked onto the sample as protectant to avoid the air oxidation in the course of sample transfer from the Shelenk bottle to the characterization equipment in the above all characterization of catalysts. The uptake data of H_2 pulse adsorption was obtained from a Micromeritics ASAP 2010 apparatus. The temperature-programmed desorption (TPD) of $CO + H_2 + C_2H_4$ (molar ratio of $CO + H_2 + C_2H_4 = 1 : 1 : 1$), temperature-programmed reduction (TPR) and H_2 pulse adsorption were also operated on the Micromeritics ASAP 2010 apparatus. The Balzers Instruments Omnistar^{TM} mass spectroscopy was used as detector for desorption species in the TPD of $CO + H_2 + C_2H_4$.

Table 1
Results of hydroformylation of 1-hexene over different catalysts in slurry-bed reactor

Catalysts	Selectivity (wt.%)			*n/i*	TOF (h^{-1})
	Aldehydes	Hexane	Hexane-2 and -3		
Rh/SiO_2	6.9	0	93.1	1.10	21
PPh_3–Rh/SiO_2	83.5	0	16.5	3.13	1011
$HRhCO(PPh_3)_3$	87.1	0	12.9	3.24	1658

Reaction conditions: $T = 373$ K; $P = 1.0$ MPa; $t = 0.5$ h; $R = 900$ r/min; the amount of used PPh_3–Rh/SiO_2 catalyst = 0.5 g; the TOF of aldehydes of the Rh/SiO_2 and PPh_3–Rh/SiO_2 catalyst was calculated on the total Rh atom on the SiO_2 support.

3. Results and discussion

3.1. Catalytic performance of PPh_3–Rh/SiO_2 catalyst for hydroformylation of 1-hexene

Table 1 shows the results of hydroformylation of 1-hexene over Rh/SiO_2, homogeneous $HRh(CO)(PPh_3)_3$ and our PPh_3–Rh/SiO_2 catalysts in the slurry-bed reactor. The isomerization of C=C bonds was dominant over the heterogeneous Rh/SiO_2 catalyst and the selectivity toward aldehyde is very low. On the contrary, the homogeneous $HRh(CO)(PPh_3)_3$ complex shows very high activity and selectivity towards aldehydes. The TOF of the homogeneous catalyst was detected as 1658 h^{-1}, which is comparable with the literature value (1652 h^{-1}) [8]. It is worth to note that the PPh_3–Rh/SiO_2 catalyst exhibits the TOF of 1011 h^{-1}, selectivity towards aldehyde of 84% and *n/i* ratio of aldehyde of 3.1, respectively, which were almost close to those of the homogeneous $HRhCO(PPh_3)_3$ counterpart and by far higher than those of the Rh/SiO_2 catalyst. This result implies that the addition of PPh_3 to Rh/SiO_2 precursor exerts a significant role on the Rh/SiO_2 and thus enhanced the catalytic performance of PPh_3–Rh/SiO_2 catalyst.

^{31}P CP-MAS NMR measurements of the products after hydroformylation over PPh_3–Rh/SiO_2 catalyst showed that there was only one peak at −6.0 ppm assigned to free PPh_3, which implied some excess PPh_3 on the PPh_3–Rh/SiO_2 catalyst leached to the solutions. The hot filtrates was also subjected to atomic absorption spectroscopy (AAS) measurements of Rh content, which exhibited very little leaching of Rh metals from the PPh_3–Rh/SiO_2 during reactions. Thus hydroformylation of olefins mainly took place on the surface of the heterogeneous PPh_3–Rh/SiO_2 catalyst.

3.2. TPR, XPS and H_2 pulse adsorption study of the Rh/SiO_2 precursor and PPh_3–Rh/SiO_2 catalyst

The TPR profile of the Rh/SiO_2 precursor shows there is only one H_2 consumption peak in the range of 322–422 K (Fig. 1). Our catalyst was reduced in the flow of the H_2 at high temperature of 573 K, which was much higher than that

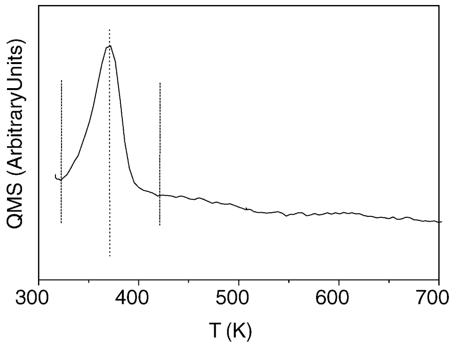

Fig. 1. TPR profile of Rh/SiO_2 catalyst.

of the TPR temperature of 422 K. Thus the chemical state of the Rh on the surface of the Rh/SiO_2 and PPh_3–Rh/SiO_2 catalyst exists as zero valent Rh metal particles. In addition, the XPS results show that the Rh^0 metal particles with a binding energy of 307.2 eV appear on the PPh_3–Rh/SiO_2 and Rh/SiO_2 sample. The uptake data of H_2 pulse adsorption has shown the dispersion of metal particles on the surface of SiO_2 is up to 67%, implying that two-third of the metals is exposed and Rh metal exists as nanoparticles.

3.3. TG and ^{31}P MAS NMR study of the PPh_3–Rh/SiO_2 catalyst

The interaction between phosphine and Rh/SiO_2 was investigated by means of TG and ^{31}P MAS NMR techniques. Fig. 2 shows the TG and its differential profiles of PPh_3–Rh/SiO_2 catalyst. On the SiO_2 sample, profile A displayed that there was a large weight loss with the temperature increased from 50 °C to ca. 100 °C due to the quick weight loss of heptanes, while there was a little weight loss due to the dehydration and dehydroxylation of SiO_2 in the range of 100–700 °C. In comparison to sample A, profile B clearly exhibited that there was weight loss from 110 to 700 °C due to the removal of PPh_3 from the PPh_3/SiO_2 sample. TG differential profile of the sample B showed that two signals appeared in the course of removal of PPh_3 with the increase of temperature. The big one was in the range of 110–290 °C, probably attributed to the removal of physically adsorbed PPh_3 ligands, and the small one is from 290 to 390 °C, probably attributed to the removal of PPh_3 ligands chemically adsorbed on the SiO_2 support. Two signals of the PPh_3–Rh/SiO_2 sample were also visible in the range of 110–290 °C and from 290 to 410 °C, respectively (Fig. 2(C)). However, it is worthy of note that the former one becomes small, but the latter one becomes big by comparison with corresponding signals in the Fig. 2(B). It implied that a certain amount of PPh_3 ligands chemically adsorbed on Rh metal particles in the PPh_3–Rh/SiO_2 catalyst, that is, chemical bond between the PPh_3 ligands and Rh particles on the Rh/SiO_2 was probably formed. From those observations, we could believe that this chemical interaction between Rh/SiO_2 and ligand is very different from those reported in the homogeneous catalyst but is similar to those reported in the heterogeneous asymmetric catalyst [18].

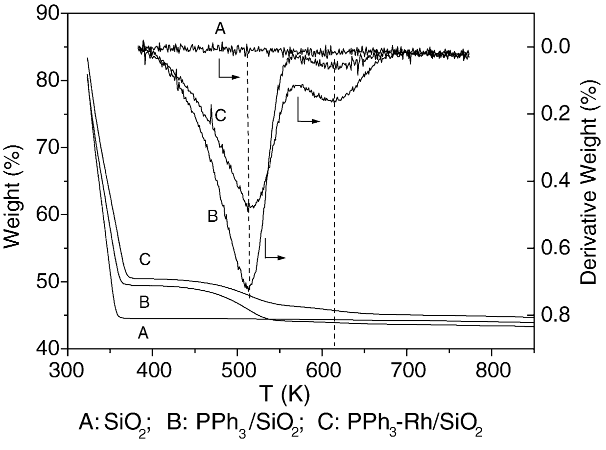

Fig. 2. Thermogravimetric analysis and TG derivative profiles of the SiO_2, PPh_3/SiO_2 and PPh_3–Rh/SiO_2 samples.

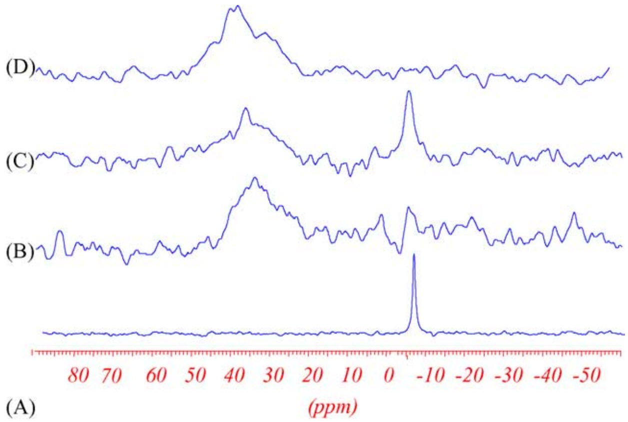

Fig. 3. ^{31}P NMR spectra of samples containing phosphines (A: PPh_3/SiO_2; B: PPh_3–Rh/SiO_2; C: PPh_3–Rh/SiO_2 treated by CO + H_2; D: $HRhCO(PPh_3)_3/SiO_2$).

The formation of chemical bond was further proven by ^{31}P MAS NMR spectra, as shown in Fig. 3. In the spectrum A, there was a sharp signal at −6.2 ppm assigned to free PPh_3 on the PPh_3/SiO_2. While in the spectrum B, a broad peak at ca. +34.1 ppm appeared and the signal at ca. −6.2 ppm became very weak when the PPh_3 ligands were added onto Rh/SiO_2. There was a broad signal at 37.2 ppm in the ^{31}P MAS NMR spectrum of $HRhCO(PPh_3)_3/SiO_2$ sample (Fig. 3(D)), which could be attributed to the arose coordination bond between Rh^+ ion and PPh_3 of rhodium complex [19]. By comparison, the chemical shift as well as the appearance of the broad peak at 37.2 ppm in the spectrum D was close to both of that at ca. +34.1 ppm in the spectrum B. This result suggested that chemical coordination bond was formed between PPh_3 and surfacial Rh metal particle on the PPh_3–Rh/SiO_2 sample. It was the first time to confirm the coordination bond between PPh_3 and Rh metal particles. When the PPh_3–Rh/SiO_2 catalyst was further treated with

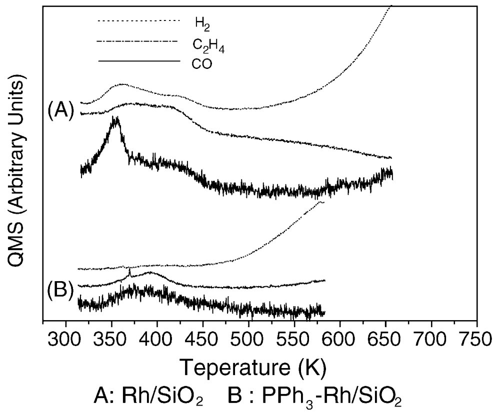

Fig. 4. CO-TPD, H_2-TPD and C_2H_4-TPD profiles of the Rh/SiO_2 and PPh_3–Rh/SiO_2 samples using $CO + H_2 + C_2H_4$ as adsorbent.

a mixture of $CO + H_2$ (denoted as PPh_3–Rh/SiO_2-syngas sample), the sharp absorption peak at −6.2 ppm became stronger and the broad peak at ca. +34.1 ppm slightly shifted to a broad signal at +36.3 ppm (Fig. 3(C)). This result implies that some of the adsorbed PPh_3 on Rh sites were released in the form of free PPh_3 as a result of substitution of CO for the adsorbed PPh_3 on the surface of Rh/SiO_2.

3.4. TPD study of the PPh_3–Rh/SiO_2 catalyst

In order to investigate the effect of addition of PPh_3 onto the Rh/SiO_2 on the adsorption state of reactant CO, H_2 and C_2H_4, the $CO + H_2 + C_2H_4$-TPD experiment was carried out. It was obvious that there were at least two desorption peaks of CO, H_2 and C_2H_4 on the Rh/SiO_2 sample at the low temperature areas (see Fig. 4). However, only one desorption peak at about 380 K of CO, H_2 and C_2H_4 was visible on the PPh_3–Rh/SiO_2 sample at the low temperature zone. This result implied that there was only each one species of CO, H_2 and C_2H_4 adsorbed on the PPh_3–Rh/SiO_2. There were a large quantity of H_2 desorption at the high temperature zone on the both of the H_2 desorption profiles of the Rh/SiO_2 and PPh_3–Rh/SiO_2 samples, which were probably ascribed to H_2 spillover on the SiO_2 supports of the two samples. It was interesting to find that signal at 383 K of C_3H_6O was also detected in the course of $CO + H_2 + C_2H_4$-TPD of PPh_3–Rh/SiO_2 catalyst, whereas nothing was found in those of Rh/SiO_2 catalyst (Fig. 5). The results suggested that the PPh_3–Rh/SiO_2 catalyzed hydroformylation of olefins with high catalytic performances on the surface of the heterogeneous catalyst.

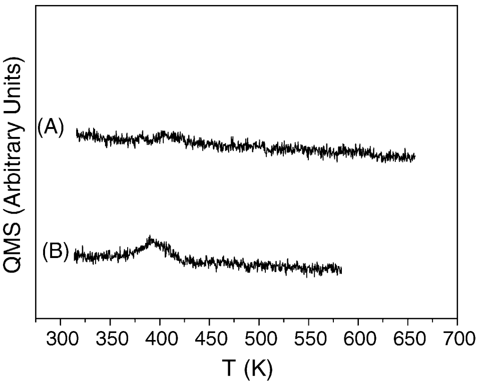

Fig. 5. C_3H_6O-TPD profiles of the Rh/SiO_2 and PPh_3–Rh/SiO_2 samples using $CO + H_2 + C_2H_4$ as adsorbent (A: Rh/SiO_2; B: PPh_3–Rh/SiO_2).

Table 2
Prospective applications of PPh_3–Rh/SiO_2 catalyst for hydroformylation of olefins

Olefin	Conversion (%)	Selectivity (%)			*n*/*i*
		Aldehyde	Paraffin	*Iso*-olefin	
Ethylene	95	99.7	0.3	–	–
1-Hexene	99.5	95.5	1.5	2.96	3.31
1-Octene	99.5	98.8	0	1.2	3.17
1-Dodecylene	98.2	94.9	0	5.10	3.33

Reaction conditions: $T = 373$ K; $P = 1.0$ MPa; $t = 4$ h; $R = 900$ r/min; the amount of used PPh_3–Rh/SiO_2 catalyst = 0.5 g. A mixture of H_2, CO and C_2H_4 was fed into the slurry reactor at 120 ml/min for ethylene.

3.5. Perspective for possible applications

A series of olefins with different carbon number were hydroformylated over PPh_3–Rh/SiO_2 catalyst, the results are shown in Table 2. It could be seen that the PPh_3 modified catalyst exhibit high conversion, selectivity for hydroformylation of olefins. This is especially important for the higher olefin, such as 1-dodecylene. The conversion of olefin was up to 98%, while 95% of the selectivity toward aldehydes with *n*/*i* higher than 3.3 is acquired. Comparing to the previous invention of the hydroformylation using biphasic catalysis, the TOF for aldehyde of the phosphine-modified Rh/SiO_2 catalyst was one or two orders of magnitude higher than that of the conventional biphasic catalysts even under lower pressure of 1 MPa [8]. Moreover, no decrease of the conversion and selectivity towards aldehydes with the increase of carbon number of olefins was observed in our experiments.

4. Conclusions

In conclusion, the hybrid PPh_3–Rh/SiO_2 catalyst for hydroformylation of olefins was prepared by doping PPh_3 onto the Rh/SiO_2. To our knowledge, it is the first successful example of PPh_3 modified rhodium heterogeneous catalyst that exhibits high activity, selectivity and easy separation for the hydroformylation of olefins. The chemical bond of the hybrid catalyst was formed between the PPh_3 ligand and Rh metal particles on the surface of SiO_2 support. All the results reveal that hydroformylation of olefins to aldehydes dominantly takes place on the surface of the hybrid catalyst. Our technique could provide a new approach to tackle the difficulty encountered with the heterogeneous catalyst with low activity and selectivity and problem associated with separation in the homogeneous catalyst from the products in the hydroformylation of olefins reaction.

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