Recyclable Heterogeneous Rh/SiO$_2$ Catalyst Enhanced by Organic PPh$_3$ Ligand

Hejun Zhu, Yunjie Ding,* Li Yan, Yuan Lu, Can Li, Xinhe Bao, and Liwu Lin
Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, P. R. China

(Received February 12, 2004; CL-040166)

Heterogeneous PPh$_3$–Rh/SiO$_2$ catalysts for hydroformylation of olefins, prepared by direct doping of phosphine onto the heterogeneous Rh/SiO$_2$ precursor, exhibited high activity and selectivity towards aldehydes, which originated from chemical coordination bond between the phosphine and Rh metal nanoparticles on the SiO$_2$ support.

Heterogeneous Rh/SiO$_2$ modified with metal oxide or alkali metal promoters for hydroformylation of olefins possesses the advantage of easy separation and recycle of catalyst from reaction system but has the disadvantages of low activity and selectivity.[1] The HRhCO(PPh$_3$)$_3$ (PPh$_3$ = triphenylphosphine) as homogeneous catalysts for hydroformylation process exhibits high activity and selectivity toward aldehydes,[2] but encounters the difficulty to separate the soluble catalyst from reaction system.[3]

Approaches for immobilization of homogeneous complex to solve this problem have been explored.[4] The water/oil biphasic process using water-soluble catalyst [HRhCO(TPPTS)$_3$] (TPPTS = triphenylphosphanyl trisulfonate) has been developed for the hydroformylation of propylene.[5] The applicability of the aqueous biphasic system is, however, strictly limited to substrates that are slightly soluble in water, such as propylene and 1-butene. Another strategy has long been attachment of the catalyst to polymer resin or silica and the separation are recyclable by a simple filtration.[6] However, low activity, selectivity, and leaching of Rh have limited the actual application of "heterogenized" catalysts in industry.

In this paper, we wish to report a new type of organic triphenylphosphine ligand promoting heterogeneous Rh/SiO$_2$ catalysts (PPh$_3$–Rh/SiO$_2$) for hydroformylation of olefins. This catalyst system was prepared by directly employing a phosphine with lone-pair electron to modify heterogeneous Rh/SiO$_2$ with an intention to get the heterogeneous catalyst with high activity, selectivity and easy separation.

Heterogeneous Rh/SiO$_2$ precursor was prepared by incipient wetness impregnation of silica with a solution of RhCl$_3$. 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. This heterogeneous Rh/SiO$_2$ precursor were introduced to the solution of phosphines in cyclohexane solvent in a Schlenk bottle (the molar ratio of P:Rh = 15:1, unless specified), then the sample was stirred for 1 h at room temperature, and lastly the solvent was evacuated under vacuum at room temperature. The black PPh$_3$–Rh/SiO$_2$ catalyst was stored under argon at room temperature. The Rh loading of Rh/SiO$_2$ was 1 wt%. The uptake data of H$_2$ pulse adsorption of the Rh/SiO$_2$ precursor has showed that the dispersion of metals on the surface of SiO$_2$ is 67% and Rh metal exists as nanoparticles.

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 selectivity toward aldehyde is very low and the turnover frequency (TOF) towards aldehydes of the Rh/SiO$_2$ catalyst is as low as 21 h^{-1}. In contrast, 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}. It is worth to note that the black 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 counterpart HRhCO(PPh$_3$)$_3$. It is surprised that its catalytic performances are 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 activity of PPh$_3$–Rh/SiO$_2$ catalyst. In addition, the PPh$_3$–Rh/SiO$_2$ catalyst was easily to be separated from the reaction systems and recycled as those of the conventional heterogeneous catalysts.

Table 1. The results of 1-hexene hydroformylation over different catalysts

Catalysts	Conv. /%	Selectivity				TOF
		Alde	Hexane	Hexene-2 and -3	n/i	
Rh/SiO$_2$	97.5	6.9	0	93.1	1.1	21
HRhCO(PPh$_3$)$_3$	18.4	87.1	0	12.9	3.2	1658
PPh$_3$–Rh/SiO$_2$	23.1	83.5	0	16.5	3.1	1011
PPh$_3$–Rh/SiO$_2$[a]	29.4	100	0	0	–	–
PPh$_3$–Rh/SiO$_2$[b]	30.6	100	0	0	–	–

[a]Rection conditions: $T = 373$ K; P = 1.0 MPa; the stirring rate was 900 RPM; Rh/Si$_2$ catalyst was tested for 4 h, the other catalysts were tested 0.5 h; In the hydroformylation of 1-hexene, the gas pressure ratio of CO and H$_2$ is 0.5 MPa:0.5 MPa. In the hydroformylation of C$_2$H$_4$, the gas pressure ratio of CO, H$_2$ and C$_2$H$_4$ is 0.33 MPa:0.33 MPa:0.33 MPa; TOF is defined as moles of aldehydes formed per mole of rhodium per hour; PPh$_3$–Rh/SiO$_2$ (3.25×10^{-2} mmol of Rh); HRh(CO)(PPh$_3$)$_3$ (2.17×10^{-2} mmol of Rh); Rh/SiO$_2$ (10.83×10^{-2} mmol of Rh); 1-hexene (15 mL); [a]The catalytic performance for hydroformylation of ethylene over PPh$_3$–Rh/SiO$_2$ in the fixed-bed reactor at 75th hour; [b]the catalytic performance for hydroformylation of ethylene over PPh$_3$–Rh/SiO$_2$ in the fixed-bed reactor at 950th hour.

Hydroformylation of ethylene over PPh$_3$–Rh/SiO$_2$ catalyst was carried out in the fixed-bed reactor at 373 K and 1.0 MPa for more than 1000 h. Some representative data are shown in Table 1. The conversion of ethylene at 75th h was almost equivalent to those at 950th h, which demonstrated good stable activity for PPh$_3$–Rh/SiO$_2$ catalyst over a long period of time. It was very important that no Rh leaching of the black PPh$_3$–Rh/SiO$_2$ catalyst was observed in the course of the operation. Another advantage was that this reaction system could be conducted in a continuous manner and the product could be very easily separated from the reactor. From above observations, we can conclude that the hydroformylation of olefin mostly takes place on the surface of the heterogeneous PPh$_3$–Rh/SiO$_2$ catalyst.

The interaction between phosphine and Rh/SiO$_2$ was investigated by means of ^{31}P MAS NMR and FTIR techniques. Figure 1 shows the ^{31}P MAS NMR spectra of the PPh$_3$/SiO$_2$, PPh$_3$–Rh/SiO$_2$ and HRhCO(PPh$_3$)$_3$/SiO$_2$ catalysts. 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. −6.0 ppm became weak when the PPh$_3$ ligands was 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 (Figure 1C), which could be attributed to the arose coordination bond between Rh$^+$ ion and PPh$_3$ of rhodium complex.[8] By comparison, the chemical shift as well as the appearance of the broad peak at 37.2 ppm in the spectrum C 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 nanoparticle on the PPh$_3$–Rh/SiO$_2$ sample.

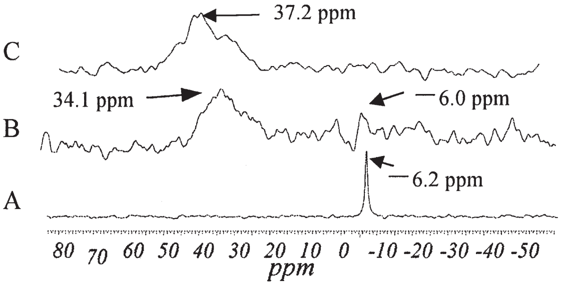

Figure 1. ^{31}P MAS NMR spectra of samples containing PPh$_3$ (the molar ratio of PPh$_3$ to Rh = 3:1) (A) PPh$_3$/SiO$_2$; (B) PPh$_3$–Rh/SiO$_2$; (C) HRhCO(PPh$_3$)$_3$/SiO$_2$.

Figure 2 shows the FTIR spectra of the CO adsorbed on the Rh/SiO$_2$ and PPh$_3$–Rh/SiO$_2$, and the rhodium–phosphine carbonyl complex. The signals at 2050 cm^{-1} and 1892 cm^{-1} were assigned to linear and bridged CO adsorbed on the Rh/SiO$_2$ (Figure 2B), respectively. In addition, gem-dicarbonyl gave bands at 2095 cm^{-1} and 2034 cm^{-1}.[9] However, there was a broad band at 2040 cm^{-1} and a small band at 1846 cm^{-1}on the PPh$_3$–Rh/SiO$_2$ (Figure 2C). They might be assigned to the linear and bridged CO adsorbed on the surface of Rh metal particle modified by PPh$_3$, respectively.

Rhodium–phosphine carbonyl complex gave the IR bands at 1980 cm^{-1} and 1940 cm^{-1} (Figure 2A), assigned to carbonyl stretching bands of homogeneous HRhCO$_2$(PPh$_3$)$_2$.[10] It was obvious that these two bands of PPh$_3$–Rh/SiO$_2$ were distinguished from those of HRhCO(PPh$_3$)$_2$, suggesting that the Rh nanoparticles active site of the PPh$_3$–Rh/SiO$_2$ was evidently different from the Rh ion active site of the HRhCO(PPh$_3$)$_2$.

The in situ reaction of the gas-solid phase hydroformylation of ethylene was carried out at 373 K under 6.7 kPa in an IR cell on the surface of PPh$_3$–Rh/SiO$_2$. From the results of Figure 2D we can see that there is no signal corresponding to propanal for 90 min on the Rh/SiO$_2$. On the contrary, a band at 1740 cm^{-1} assigned to carbonyl stretching of propanal and very weak bands at 1760 cm^{-1} and 2870 cm^{-1} assigned to C–H of aldehyde appeared for 5 min for PPh$_3$–Rh/SiO$_2$ (Figure 2E). The active CO species at 2045 cm^{-1} for hydroformylation of ethylene was linear CO adsorbed on the Rh metal particle modified by PPh$_3$. This result further confirmed that hydroformylation of ethylene occurred on the heterogeneous PPh$_3$–Rh/SiO$_2$ catalyst, not the derived homogeneous rhodium–phosphine species.

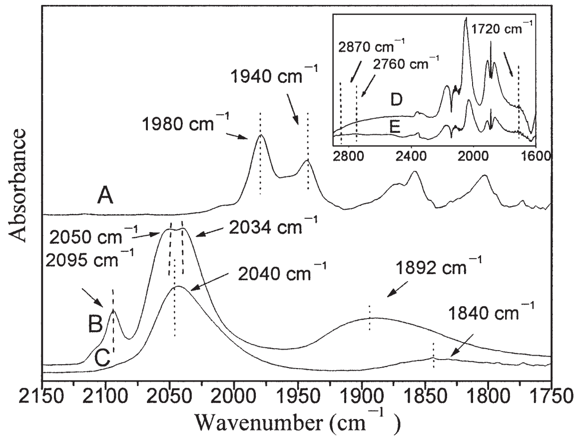

Figure 2. The FTIR spectra of the CO absorbed Rh/SiO$_2$ and PPh$_3$–Rh/SiO$_2$ (the molar ratio of PPh$_3$ to Rh = 3:1) and the rhodium–phosphine carbonyl complex, and the in situ hydroformylation of CO/H$_2$/C$_2$H$_4$ on Rh/SiO$_2$ and PPh$_3$–Rh/SiO$_2$ in an IR cell (A) rhodium–phosphine carbonyl complex; (B) Rh/SiO$_2$; (C) PPh$_3$–Rh/SiO$_2$; (D) CO/H$_2$/C$_2$H$_4$ hydroformylation on RhSiO$_2$ in an IR cell after 90 min; (E) CO/H$_2$/C$_2$H$_4$ hydroformylation on PPh$_3$–Rh/SiO$_2$ after 5 min.

In conclusion, the heterogeneous PPh$_3$–Rh/SiO$_2$ catalysts for hydroformylation of olefins, prepared by modifying the Rh/SiO$_2$ precursor with organic phosphines, demonstrated the advantages of high activity, selectivity towards aldehydes and easy separation. The chemical bond of the catalysts was not only obviously distinguished from those of hererogeneous Rh/SiO$_2$ catalyst, but also different from those of homogeneous counterparts.

This work was financially supported by the Science and Technology Ministry of China (Grant no. 2003CB615803)

References

1 a) M. Ichikawa, A. J. Lang, D. F. Shriver, and W. M. H. Sachtler, *J. Am. Chem. Soc.*, **107**, 7216 (1985). b) Y. Izumi, K. Asakura, and Y. Iwasawa, *J. Catal.*, **132**, 566 (1991). c) N. Takahashi, S. Hasegawa, N. Hanada, and M. Kobayashi, *Chem. Lett.*, **1983**, 945. d) S. Naito and M. Tanimoto, *J. Chem. Soc., Chem. Commum.*, **1989**, 1403. e) M. A. Brundage and S. S. C. Chuang, *J. Catal.*, **174**, 164 (1998). f) F. G. A. Ven den Berg, J. H. Glezer, and W. M. H. Sachtler, *J. Catal.*, **93**, 340 (1985).
2 D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, **12**, 3133 (1968).
3 B. Cornils, W. A. Herrmann, and M. Rasch, *Angew. Chem., Int. Ed. Engl.*, **33**, 2144 (1994).
4 D. J. Cole-Hamilton, *Science*, **299**, 1702 (2003).
5 a) E. G. Kuntz, *CHEMTECH*, **17**, 570 (1987). b) W. A. Herrmann, C. W. Kohlpaintner, H. Bahrmann, and W. Konhol, *J. Mol. Catal. A: Chem.*, **73**, 191 (1992). c) J. P Arhancet, M. E. Davis, J. S. Merola, and B. E. Hanson, *Nature*, **339**, 454 (1989). d) D. Koch and W. Leitner, *J. Am. Chem. Soc.*, **120**, 13398 (1998). e) I. T. Horváth, *Catal. Lett.*, **6**, 43 (1990). f) Z. L. Jin, X. L. Zheng, and B. Fell, *J. Mol. Catal. A: Chem.*, **116**, 55 (1997). g) Y. Chauvin, L. Mussmann, and H. Oliver, *Angew. Chem., Int. Ed. Engl.*, **34**, 2698 (1996). h) H. J. Zhu, Y. J. Ding, H. M. Yin, L. Yan, J. M. Xiong, Y. Lu, H. Y. Luo, and L. W. Lin, *Appl. Catal., A*, **245**, 111 (2003).
6 a) G. O. Evans, C. U. Pittmann, and R. Mcmillan, Jr., *J. Organomet. Chem.*, **67**, 295 (1974). b) J. Hjortkjaer, M. S. Scurrell, and P. Simonsen, *J. Mol. Catal. A: Chem.*, **73**, 191 (1979). c) F. R. Hartley, "Supported Metal Complexes," ed. by D. Dordrecht, Reidel Publishing Company (1985). d) A. J. Sandee, L. A. van der Veen, J. N. H. Reek, P. C. J. Kamer, M. Lutz, A. L. Spek, and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed. Engl.*, **38**, 3231 (1999). e) K. Mukhopadhyay and R. V. Chaudhari, *J. Catal.*, **213**, 73 (2003).
7 C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
8 Y. Zhang, Y. Z. Yuan, Z. Cheng, G. D. Lin, and H. B. Zhang, *J. Xiamen Univ., (Natural science)* **37**, 228 (1998).
9 A. C. Yang and C. W. Garland, *J. Phys. Chem.*, **61**, 1504 (1957).
10 D. E. Morris and H. B. Tinker, *CHEMTECH*, **2**, 554 (1972).

Published on the web (Advance View) April 24, 2004; DOI 10.1246/cl.2004.630