

Water/Oil Biphasic Hydroformylation of Higher Olefins over a TPPTS-Rh/SiO₂ Catalyst

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Abstract: A novel TPPTS-Rh/SiO₂ catalyst, prepared by directly modifying a heterogeneous high-surface-area Rh/SiO₂ catalyst with water-soluble TPPTS ligands, could decrease the resistance of mass transfer in water/oil biphasic media for the hydroformylation of higher olefins. The catalytic performance for hydroformylation on this biphasic TPPTS-Rh/SiO₂ catalyst system was higher than those of the traditional biphasic HRhCO(TPPTS)₃ systems, owing to the chemical bonds between the highly dispersed Rh metal particles and the TPPTS ligands. The catalyst system is applicable for hydroformylation of higher olefins such as 1-dodecene.

Key words: hydroformylation, higher olefins, TPPTS-Rh/SiO₂ catalyst

1. Introduction

Hydroformylation of higher olefins (C₆ or higher) is a highly interesting field both industrially and academically [1–3]. One of the most important developments of the last two decades in hydroformylation chemistry was the development in water/oil biphasic homogeneous catalysis. However, the applicability of the aqueous biphasic system is strictly limited to substrates that are slightly soluble in water, such as propylene and 1-butene [2].

One of the approaches to overcome this difficulty has been made by utilizing the supported aqueous-phase (SAP) catalysts, in which the HRhCO(TPPTS)₃ is located in the water film of the pores in the high-surface-area SiO₂ (HRhCO(TPPTS)₃/SiO₂) [4–5]. We have reported a new type of SAP catalyst for catalytic hydroformylation of 1-hexene prepared by modifying the heterogeneous Rh/SiO₂ catalyst with TPPTS ligands (TPPTS-Rh/SiO₂) in the water film of the pores in the support. The catalytic performance of the

TPPTS-Rh/SiO₂ was comparable to those of the HRhCO(TPPTS)₃/SiO₂ catalysts [6]. However, the small amount of water in the SAP catalysts is easy to get lost, thus leading to decreases in catalytic activity and stability. Here, we report on a new catalyst system of TPPTS-Rh/SiO₂, which possesses simultaneously water/oil bi-phase for hydroformylation of higher olefin, as compared with the dry TPPTS-Rh/SiO₂ catalyst in a water phase. The schematic of the biphasic TPPTS-Rh/SiO₂ catalyst system is shown in Figure 1.

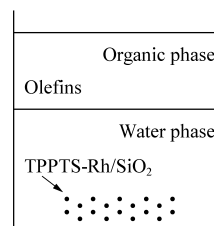


Figure 1. The schematic of the water/oil biphasic TPPTS-Rh/SiO₂ catalyst system for hydroformylation of higher olefins

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2. Experimental

2.1. Catalyst preparation

The Rh metal loadings of all Rh/SiO₂ catalysts were 1 wt%. These supported Rh catalysts (Rh/SiO₂) were prepared by impregnating a silica support with an aqueous RhCl₃ solution, then dried first at room temperature, subsequently at 393 K, and finally calcined at 573 K for 3 h. The samples were then reduced in flowing H₂ at 573 K for 3 h. TPPTS ligands were then added to 3 ml of water and stirred until it dissolved completely. To this solution 0.3 g of the Rh/SiO₂ supported catalyst was added (the molar ratio of P:Rh=15, unless specified otherwise), and the mixture was stirred for 0.5 h, and then the solution was removed, and the sample evacuated for 2 h. The final dry samples had to be kept under an Ar atmosphere. The above manipulations should be carefully carried out to avoid contact of the samples with air.

2.2. Catalyst test

Catalytic evaluations were performed in a 300 ml slurry-bed reactor. After 60 ml water, 15 ml olefins and the TPPTS-Rh/SiO₂ catalyst were carefully introduced into the reactor under Ar atmosphere, the reactor was purged six times with a mixture of CO/H₂ (H₂/CO=1), then the reaction pressure was adjusted to 1.0 MPa (unless specified otherwise), and the reactor was heated to the reaction temperature of 373 K. The reaction mixture was stirred at 900 RPM for 0.5 h. The products of hydroformylation were analyzed by a Varian 3800 gas chromatograph with a SE-30 capillary column.

2.3. Catalyst characterization

³¹P-MAS NMR experiments were performed on a Bruker DRX-400 Spectrometer. Phosphorus-31 NMR chemical shifts are reported relative to 85%³¹P.

3. Results and discussion

3.1. Comparison of catalytic performances of different kinds of catalyst

Comparing with the SAP TPPTS-Rh/SiO₂ catalysts, one of the remarkable advantages of the biphasic TPPTS-Rh/SiO₂ catalysts is that the large amount of water existing in the latter system will not lose easily in long period reaction operations, so that its catalytic activity can be kept very stable. This is consistent with that of the biphasic HRhCO(TPPTS)₃ catalyst. Hydroformylation results of 1-hexene over heterogeneous Rh/SiO₂, homogeneous HRhCO(TPPTS)₃ and heterogeneous TPPTS-Rh/SiO₂ catalysts in water/oil two phases are listed in Table 1. It can be seen that the isomerization of C=C bonds is dominant over the heterogeneous Rh/SiO₂ catalyst, but the selectivity towards aldehydes is very low. The turnover frequency (TOF) towards aldehydes on the Rh/SiO₂ catalyst is only 13 h⁻¹. On the contrary, the water soluble homogeneous HRhCO(TPPTS)₃ complex shows high activity and selectivity towards aldehydes. The TOF of this homogeneous catalyst was determined to be 752 h⁻¹. It is worth to note that the TPPTS-Rh/SiO₂ catalyst gave a TOF of 555 h⁻¹, while the selectivity towards aldehydes was 62.1%, and the *n/i* (normal/iso) ratio of the aldehydes was 3.8. These data are higher than those of the Rh/SiO₂ catalyst, but are almost equal to those of the water soluble counterpart HRhCO(TPPTS)₃. These results imply that the addition of TPPTS to the Rh/SiO₂ precursor can affect the catalytic properties of the Rh/SiO₂.

Table 1. Results of hydroformylation of 1-hexene over different catalysts in two phases

Catalyst	Conversion (%)	Selectivity (%)			<i>n/i</i>	TOF (h ⁻¹)
		Aldehyde	Hexane	Hexene-2 and -3		
Rh/SiO ₂	95.6	4.5	0	95.5	1.0	13
HRhCO(TPPTS) ₃	28.7	61.3	2.4	37.8	4.1	752
TPPTS-Rh/SiO ₂	10.3	62.1	7.7	30.2	3.8	555

Reaction conditions: *T*=373 K, *p*=1.0 MPa, *t*=0.5 h, *R*=900 r/min. The TOF of aldehydes of the Rh/SiO₂ and PPh₃-Rh/SiO₂ catalysts were calculated on the exposed Rh atoms on the SiO₂ support. The TOF of aldehydes of the HRhCO(TPPTS)₃ catalyst was calculated on the total Rh ions. The used Rh/SiO₂ catalyst was 1.5 g. The content of used HRhCO(TPPTS)₃ catalyst was 162 ppm (molar ratio of Rh/1-hexene).

3.2. ^{31}P NMR spectra

^{31}P NMR spectra for the samples of TPPTS adsorbed on SiO_2 , TPPTS-Rh/ SiO_2 , and $\text{HRhCO}(\text{TPPTS})_3$ adsorbed on SiO_2 are shown in Figure 2.

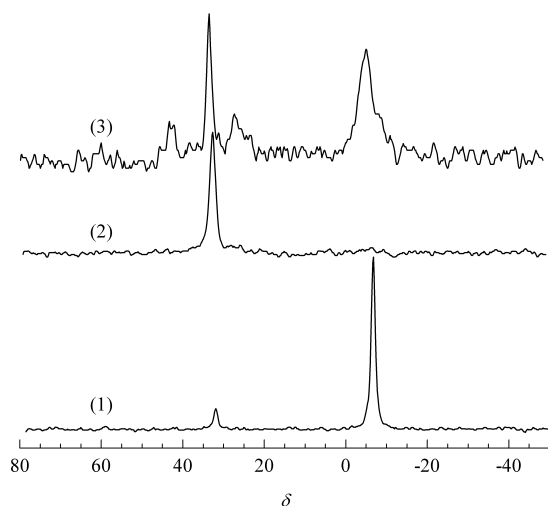


Figure 2. ^{31}P NMR spectra of different samples containing TPPTS

(1) TPPTS adsorbed on SiO_2 , (2) TPPTS-Rh/ SiO_2 , (3) $\text{HRhCO}(\text{TPPTS})_3$ adsorbed on SiO_2

Spectrum (1) has a big and sharp absorption peak at -6.2 ppm, and a small peak at 32.8 ppm, assigned respectively to free TPPTS and oxidized TPPTS on the TPPTS/ SiO_2 sample. For the TPPTS-Rh/ SiO_2 catalyst, the peak at 33.0 ppm appeared and the peak at -6.2 ppm disappeared in spectrum (2). In spectrum (3), four signals were seen at 42.0 , 33.2 , 26.9 and -6.2 ppm, and these are assigned to $\text{HRhCO}(\text{TPPTS})_3$, $\text{RhCO}(\text{TPPTS})_2$, an unidentified species, and free TPPTS, respectively [5]. The latter three species for the sample of $\text{HRhCO}(\text{TPPTS})_3$ adsorbed on SiO_2 were originated from partial decomposition of the

$\text{HRhCO}(\text{TPPTS})_3$ owing to the effect of the pores of the support. By comparing the spectra, we can conclude that chemical bonds might be formed between the highly dispersed Rh particles and the TPPTS ligands in the TPPTS-Rh/ SiO_2 catalyst, which was similar to the case of $\text{Rh}(\text{CO})(\text{TPPTS})_2$ in the sample of $\text{HRhCO}(\text{TPPTS})_3$ adsorbed on SiO_2 . This was in good agreement with the result of the SAP TPPTS-Rh/ SiO_2 catalyst system [6]. Thus, the hydroformylation reaction mainly occurred with high selectivity and activity towards aldehydes on the surface of the TPPTS-Rh/ SiO_2 catalyst.

3.3. The effect of reaction pressure

Table 2 shows the effect of high reaction pressure on the catalytic performance of the TPPTS-Rh/ SiO_2 catalyst in water-oil bi-phases. For comparison, a $\text{HRhCO}(\text{TPPTS})_3$ catalyst was also investigated. As the reaction pressure was elevated from 1.0 MPa to either 4.0 or 7.0 MPa, the activity and selectivity towards aldehydes on the TPPTS-Rh/ SiO_2 catalyst increased greatly, which was rather similar to the $\text{HRhCO}(\text{TPPTS})_3$ catalyst. It was worth to note that the TOF for aldehydes on the TPPTS-Rh/ SiO_2 catalyst at 7.0 MPa was as high as 1614 h^{-1} , which was even higher than that of the traditional biphasic $\text{HRhCO}(\text{TPPTS})_3$ catalyst. This might be resulted from the fact that the high-surface-area heterogeneous TPPTS-Rh/ SiO_2 catalyst in the water phase could provide a larger space for the reaction of 1-hexene in the organic phase than in the homogeneous $\text{HRhCO}(\text{TPPTS})_3$ catalyst, thus eliminating the limit of mass transfer at a high pressure of 7.0 MPa. However, the n/i ratio of aldehydes on the TPPTS-Rh/ SiO_2 catalyst decreased somewhat at high pressures, which was also similar to the case of the $\text{HRhCO}(\text{TPPTS})_3$ catalyst.

Table 2. The effect of pressure on the catalytic performances for hydroformylation on the TPPTS-Rh/ SiO_2 and $\text{HRhCO}(\text{TPPTS})_3$ catalysts in water-oil bi-phases

Catalyst	Pressure (MPa)	Conversion (%)	Selectivity (%)			n/i	TOF (h^{-1})
			Aldehyde	Hexane	Hexene-2 and -3		
TPPTS-Rh/ SiO_2	1.0	10.2	62.1	7.7	30.2	3.8	555
	4.0	18.2	77.9	4.0	18.2	3.4	1246
	7.0	24.3	70.3	7.2	22.5	2.9	1614
$\text{HRhCO}(\text{TPPTS})_3$	1.0	28.7	61.3	2.4	37.8	4.1	752
	4.0	32.2	71.3	0	28.7	3.0	979
	7.0	22.7	88.6	1.8	9.6	2.7	1074

3.4. The perspective for possible applications

Hydroformylation of 1-octene and 1-dodecene can be converted into a large number of useful plasticizer and detergent intermediates [2]. We have further investigated the hydroformylation of these olefins at 7.0 MPa, as shown in Table 3. It was found that, with the increase of the carbon chain number of the substrate from C₆ to C₈ and C₁₂, the catalytic activity of higher olefins hydroformylation over the biphasic TPPTS-Rh/SiO₂ catalyst system decreased from 1614 to 1396 and 952 h⁻¹, respectively. However, it has been re-

ported that the reactivity in hydroformylation of the higher olefins dropped drastically in orders of magnitude with the increase of carbon chain number of the substrate over the biphasic HRhCO(TPPTS)₃ catalyst system[3]. Therefore, the extent of decrease in catalytic activity over the TPPTS-Rh/SiO₂ catalyst in biphasic system was very minor in comparison with that of the HRhCO(TPPTS)₃ catalyst. Thus, it was quite prospective that the biphasic TPPTS-Rh/SiO₂ catalyst system can be applied for hydroformylation of higher olefins.

Table 3. Results of hydroformylation of higher olefins over TPPTS-Rh/SiO₂ catalyst in two phases

Reactant	Conversion (%)	Selectivity (%)			<i>n</i> / <i>i</i>	TOF (h ⁻¹)
		Aldehyde	Hexane	Hexene-2 and -3		
1-Hexene	24.3	70.3	7.2	22.5	2.9	1614
1-Octene	32.3	61.2	0	38.8	2.7	1396
1-Dodecene	27.2	57.9	0	42.1	2.9	952

4. Conclusions

The biphasic TPPTS-Rh/SiO₂ catalyst does not have the problem of losing water. It is a new type of catalyst system for higher olefins hydroformylation of high activity and selectivity. Unlike the biphasic HRhCO(TPPTS)₃ catalyst that is soluble in the water phase, the TPPTS-Rh/SiO₂ catalyst is immiscible in water. The chemical coordination bonds between the highly dispersed Rh particles and the TPPTS ligands are responsible for its high catalytic activity for the hydroformylation of olefins. It is an important fact that the TPPTS-Rh/SiO₂ catalyst in biphasic system is applicable for the hydroformylation of higher olefins, such as 1-dodecene, with activity far higher than that of the biphasic HRhCO(TPPTS)₃ catalyst. This might be due to the fact that the high-surface-area Rh/SiO₂ provided very large space for the hydroformylation of higher olefins, which can decrease the resistance of mass transfer of the hydrophobic higher olefins and products, thus enhances the activity of

hydroformylation. Therefore, the water/oil biphasic TPPTS-Rh/SiO₂ catalyst for higher olefins hydroformylation shows a broad prospect for applications in oxo processes.

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References

- [1] Kuntz E G. *Chemtech*, 1987, **17**(9): 570
- [2] Cornils B, Herrmann A, Rasch M. *Angew Chem Int Ed Engl*, 1994, **33**(21): 2144
- [3] Horvath I T. *Catal Lett*, 1990, **6**(1): 43
- [4] Arhancet J P, Davis M E, Merola J S et al. *J Catal*, 1990, **121**(2): 327
- [5] Arhancet J P, Davis M E, Hanson B E et al. *J Catal*, 1991, **129**(1): 94
- [6] Zhu H J, Ding Y J, Yin H M et al. *Applied Catal A*, 2003, **245**(1): 111