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Application of a new amphiphilic phosphine in the aqueous biphasic catalytic hydroformylation of long chain olefins

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ABSTRACT

The preparation of a new surface-active sulfonated phosphine and its catalytic performance in aqueous biphasic hydroformylation of long chain olefins were reported. The amphiphilic phosphine: sodium salt of sulfonated *n*-$C_{12}H_{25}O$ $C_6H_4P(C_6H_4$-*p*-$CH_3O)_2$ (DMOPPS) was prepared by sulfonation of the hydrophobic phosphine DMOPP in concentrated H_2SO_4 under N_2 atmosphere at 30 °C for about 5 h. The rhodium complex, $RhCl(CO)(TPPTS)_2$ [TPPTS = $P(C_6H_4$-*m*-$SO_3Na)_3$], was used as the catalyst precursor. The catalytic active species with the DMOPPS as ligand was in situ formed by adding DMOPPS to the $RhCl(CO)(TPPTS)_2$ catalyst precursor. The surface-activity and micelle-forming property of this new amphiphilic phosphine were confirmed by using cryogenic transmission electron microscope (Cryo-TEM). Under the same conditions, the biphasic hydroformylation of 1-decene using DMOPPS as ligand was compared with that using traditional TPPTS as ligand. The catalysis system using DMOPPS was also compared with the previous Rh-TPPTS-surfactant [$C_{12}H_{25}N(CH_3)_3I$ (DTAI)] system. Some reaction parameters such as stirring rates, alkyl chain length of olefins, the molar ratio of phosphine/rhodium, and the catalyst recycle were also studied in detail. The results showed that the ligand DMOPPS exhibited a micelle-forming property that could significantly enhance the hydroformylation reaction rate of long chain olefin. Moreover, the surface-active phosphine may also stabilize the aqueous/oil phase boundary, which could enhance the biphasic catalytic reaction rates.

1. Introduction

Since the Ruhrchemie/Rhone Poulenc process (RCH/RP process, an aqueous/organic biphasic catalysis system) was successfully developed and applied in the hydroformylation of propene [1], the aqueous/organic biphasic catalysis has attracted extensive attentions. Its efficiency in the separation and recycle of noble catalyst and its environmentally benign benefits have been widely acknowledged. However, the performance was quite discouraging when the RCH/RP process was extended to the hydroformylation of long chain olefins because of their negligible solubility in water, resulting in an extremely low reaction rate.

To solve this problem, a number of efforts have been devoted to finding feasible solutions to significantly increase the reaction rates. These efforts include the addition of co-solvent [2], co-ligand [3], amphiphilic phosphine [4–7], modified cyclodextrin [8,9], and surfactant [10–15] to the hydroformylation reaction system. A novel supported aqueous-phase catalyst [16,17] has also been tried to immobilize the catalyst and enhance the reaction rate. Among these methods, using amphiphilic phosphine is very interesting because it simplifies the reaction system by incorporating the surface-active property and the coordination ability into the same phosphine ligand. The catalysis properties of several amphiphilic phosphines have been studied in the aqueous biphasic hydroformylation of olefins. Most of them bear the characteristic that the hydrophilic group (phosphonate or sulfonate) and the phosphorus atom are on the two ends of the long alkyl chain. Some typical examples include the Bischoff group's phosphonate-phosphines [18], the Hanson group's sulfonated tris(ω-phenylalkyl)phophines [5] and the Goedheijt group's amphiphilic diphosphines [6]. However, the amphiphilic phosphine with the hydrophilic groups and phosphorus atom on the same end of the carbon chain was rarely reported [19]. The structure of the latter type of amphiphilic ligand can expose the phosphorus atom directly to the aqueous phase when this kind of ligand is dissolved in water and a micelle

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structure forms. This structural arrangement can increase the reaction activity, which has already been verified in our previous report [20]. Here we report the synthesis of a novel amphiphilic phosphine (sodium salt of sulfonated n-$C_{12}H_{25}OC_6H_4P$ (C_6H_4-p-$CH_3O)_2$, DMOPPS) which has the phosphorus atom and the hydrophiphilic group (sulfonate) on the same end of the carbon chain. The catalysis properties of DMOPPS in the hydroformylation of long chain olefins are also investigated.

2. Experimental

2.1. Materials

TPPTS [P(m-$C_6H_4SO_3Na)_3$] and the catalyst precursor $RhCl(CO)(TPPTS)_2$ were prepared according to our previous report [21]. 1-Decene (Sigma, 96%), 1-dodecene (Across, 93–95%), 1-tetradecene (Sigma, 99%), 1-hexadecene (Fluka, 99%), *N*,*N*-dimethyldodecan-1-amine (C.P), iodomethane (C.P) were commercially obtained and used without further purification. Hydrogen (99.99%) and carbon monoxide (99.9%) were mixed directly with the molar ratio of 1:1.

The hydrophobic phosphine ligand, n-$C_{12}H_{25}OC_6H_4P$ (C_6H_4-p-$CH_3O)_2$ (DMOPP), was synthesized according to our previous report [22] and characterized by ^{1}H NMR (recorded on a Flucker 400 NMR instrument) and ^{31}P NMR as following:

^{1}H NMR, δ = ($CDCl_3$): 0.801 (t, 3H); 1.185 (m, 16H); 1.311 (m, 2H); 1.689 (m, 2H); 3.714 (s, 6H); 3.856 (t, 2H); 6.775 (m, 3H); 7.127 (m, 3H) and ^{31}P NMR, δ = ($CDCl_3$): −9.712.

Sulfonation of DMOPP was performed according to the method [23] with some modifications. A typical process is as follows: DMOPP was sulfonated with concentrated H_2SO_4 under N_2 atmosphere at 30 °C for about 5 h. The resultant solution was neutralized in ice-water bath by 40% (w/w) aqueous NaOH until the pH of the solution was around 8. Then deoxygenated ethanol was added repeatedly into the solution to precipitate Na_2SO_4. The removal of the solvent under vacuum afforded the ligand, DMOPPS, with a yield of 75.3%. The product was a mixture of phosphines with different sulfonation degree as in the ^{31}P NMR, the chemical shift of P is −10.37 and −10.83 ppm. The ^{31}P NMR showed no oxidation by-product (see Fig. 1).

2.2. TEM observation of micelle image of DMOPPS in aqueous solution

Negative staining was used to observe the micelle image of DMOPPS in aqueous solution (4.0 mmol/L) containing $RhCl(CO)(TPPTS)_2$ (1.0 mmol/L) by a JEM-1200EX TEM operating at 100 keV. A 300 mesh copper grid coated with carbon formvar was soaked in the DMOPPS solution for about 60 min. The grid was drained on absorbent tissues, and then the grid was stained with a drop of a 2% (w/v) solution of phosphotungstic acid. After 10 min, the liquid drop was removed with filter paper and the resultant stained sample was scanned with JEM-1200EX TEM.

2.3. Hydroformylation

The hydroformylation reactions were carried out in a 60 mL stainless autoclave with a magnetic stirrer. The catalysis-active species with the DMOPPS ligand was in situ formed by adding DMOPPS to the $RhCl(CO)(TPPTS)_2$ catalyst precursor. A typical reaction procedure was conducted as follows: rhodium catalyst, amphiphilic phosphine, surfactant, water and substrate (olefin) were added into the autoclave. Then the autoclave was evacuated and purged with syngas three times. When the temperature reached the desired value, syngas was introduced with an initial pressure of 3.0 MPa. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water to ambient temperature.

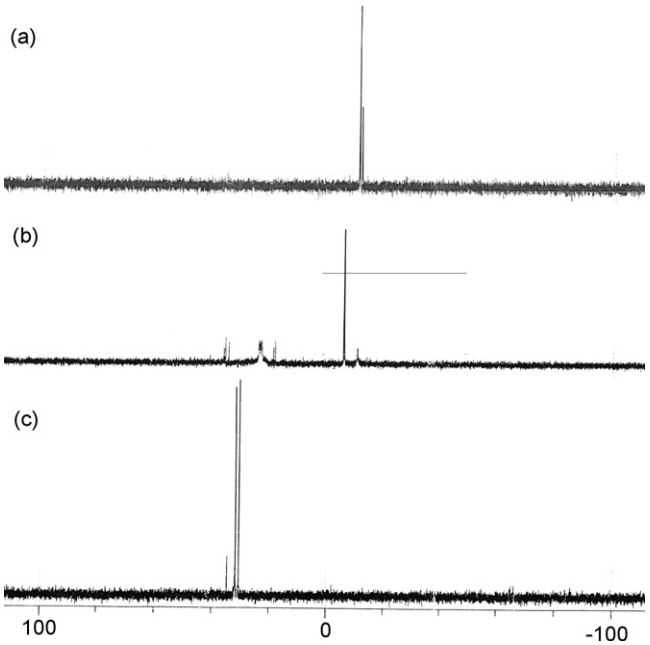


Fig. 1. Ligand exchange of TPPTS with DMOPPS tested by ^{31}P NMR (D_2O, 160MHz, 25 °C). (a) The ^{31}P NMR spectrum of DMOPPS, (b) the ^{31}P NMR spectrum of the mixture of DMOPPS and $RhCl(CO)(TPPTS)_2$ (the molar ratio of DMOPPS to $RhCl(CO)(TPPTS)_2$ is 4) and (c) the ^{31}P NMR spectrum of $RhCl(CO)(TPPTS)_2$.

An HP 1890 series II gas chromatography (Hewlett Packard, Palo Alto, CA) equipped with a flame ionization detector was used. The separation was done on a SE-30 (30 m × 0.32 mm, d.f. 0.25 μm) fused silica capillary column.

3. Results and discussion

3.1. Effect of stirring rate

The hydroformylation reactions of 1-decene at 100 °C and 3.0 MPa were performed with $RhCl(CO)(TPPTS)_2$ as catalyst precursor and phosphine DMOPPS as the modifying ligand. The concentration of $RhCl(CO)(TPPTS)_2$ was 0.96 mmol/L, and the molar ratio of 1-decene to rhodium was 1.875.

In the preliminary tests, the influences of stirring rates on the hydroformylation conversion and selectivity were investigated by screening the stirring rates at 400, 600 and 1000 rpm, respectively. The other reaction conditions were set constant. The results shown in Table 1 clearly indicate that the hydroformylation of 1-decene proceeds slowly under lower stirring rates. Because the substrate 1-decene (in organic phase) and catalyst (in aqueous phase) are dissolved in two immiscible phases, the stirring rate certainly plays a pivotal role in breaking the mass transportation limitation and enhancing the reaction rate. Therefore, the lower stirring rate at 400 rpm only led to lower reaction conversion. However, the increase in stirring rates from 400 to 600 rpm substantially enhanced both the conversion and the selectivity. The reaction rates depend on the stirring rates, particularly when the stirring rates are low. This observation suggests that in this biphasic catalysis system, the reaction may, to some degree, take place at the aqueous/oil phase boundary [24]. The introduction of the surface-active sulfonated phosphine could stabilize the interface between the aqueous and oil phases by reducing the surface tension, whereby

Table 1
Effects of the stirring rate on the reaction[a]

Stirring rate (rpm)	Con. (%)[b]	$S_{ald.}$ (%)[c]	S_{iso} (%)[d]	S_{alk} (%)[e]	L/B[f]	TOF (h^{-1})[g]
400	53.9	49.4	35.3	15.3	2.5	249.2
600	93.4	74.5	18.4	7.1	2.2	652.3
1000	98.4	75.4	17.3	7.3	2.4	695.6

[a] *Reaction conditions*: [$RhCl(CO)(TPPTS)_2$] = 0.96 mmol/L, $V_{(H_2O)}$ = 2.5 mL, n(olefin)/n(Rh) = 1875, 3.0MPa (Syn gas), 100 °C, 2 h.
[b] Conversion of olefin.
[c] Selectivity to aldehyde.
[d] Selectivity to olefin isomerization by-product.
[e] Selectivity to hydrogenation by-product.
[f] Molar ratio of linear to branched aldehyde.
[g] Moles of converted olefin per mole of rhodium and per hour.

the phosphine plays a role in stabilizing the interface like a regular surfactant does.

It is interesting that the side reaction of olefin hydrogenation was also significantly inhibited with the increase in stirring rate. The chemoselectivity for aldehyde production was augmented from 49.4% with the stirring rate at 400 rpm to 74.5% when stirred at 600 rpm. This means that at a higher stirring rate, the more desirable product, aldehyde, was generated in the hydroformylation reaction. However, the regioselectivity toward linear aldehyde (L/B value) was barely influenced by increasing the stirring rate. A further increase in stirring rate slightly affected the reaction; no significant changes in reaction rate and selectivity were observed. Consequently, the stirring rate of 600 rpm was selected as a standard stirring rate in all the following experiments.

3.2. Effect of the molar ratio of P/Rh

The existence of the electron donor alkyloxyl-group endows DMOPPS a stronger coordination ability and a tendency to displace TPPTS from $RhCl(CO)(TPPTS)_2$ and hence form the complex $RhCl(CO)(DMOPPS)_2$ (Scheme 1). This argument could be verified by ^{31}P NMR experiment (Fig. 1). The chemical shift of P atom in $RhCl(CO)(TPPTS)_2$ is at 31.56 ppm and the chemical shift is at −10.37 and −10.83 ppm in DMOPPS. However, after the addition of the ligand DMOPPS to the $RhCl(CO)(TPPTS)_2$ solution (molar ratio of DMOPPS to $RhCl(CO)(TPPTS)_2$ is 4), the signals at both the 31.56 ppm and the −10.83 ppm disappeared. Moreover, the signal at −10.37 ppm diminished and several new signals emerged simultaneously. The new signal at −5.74 ppm could be designated to the chemical shift of ligand TPPTS, and the signals at 23.8 ppm and 18.3 ppm might correspond to the newly-formed catalytic species $RhCl(CO)(DMOPPS)_2$. This rhodium complex may form different catalytic active species (Scheme 1) under the hydroformylation conditions. The concentration of phosphine DMOPPS can influence the distribution of different kinds of catalytic active species and thus influence the catalyst properties. As a result, the influences of the molar ratio of DMOPPS to Rh on the reaction were studied. As seen in Fig. 2, when the molar ratio of DMOPPS to rhodium (P/Rh)

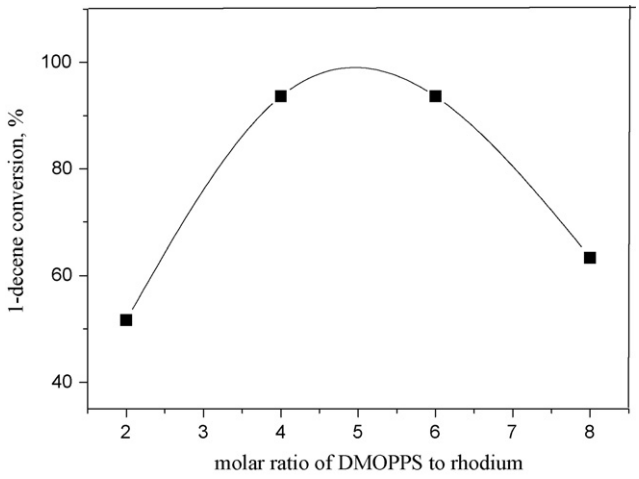
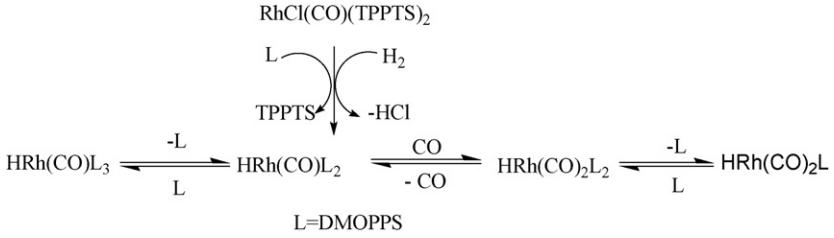


Fig. 2. Effects of the molar ratio of DMOPPS to rhodium on 1-decene conversion rates. *Reaction conditions*: [$RhCl(CO)(TPPTS)_2$] = 0.96 mmol/L, $V_{(H_2O)}$ = 2.5 mL, $n_{(olefin)}/n_{(Rh)}$ = 1875, 3.0 MPa (Syn gas), 100 °C, 600 rpm, 2 h.

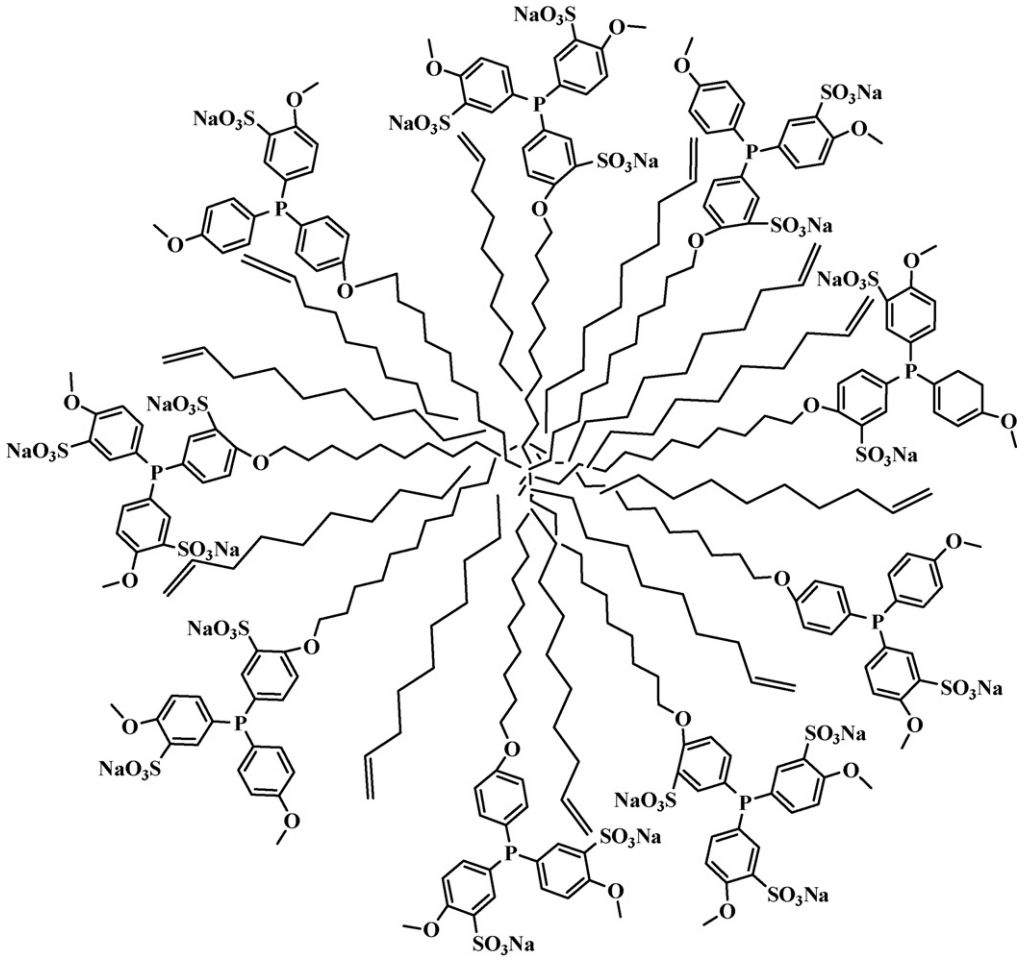
increased from 2 to 8, the conversions of 1-decene firstly went up quickly and then reached a maximum. But the further increase in P/Rh ratio led to a drastic decrease in the conversion rate. The molar ratios of DMOPPS to rhodium at 4 and 6 correspond to the concentration of DMOPPS at 3.8 and 5.7 mmol/L, respectively. The CMC (critical micelle concentration) of DMOPPS might be between these two concentration values. The DMOPPS could aggregate to form micelle in aqueous phase (Scheme 2), which was confirmed by the TEM experiment (Fig. 3). The formation of anionic micelle could solubilize 1-decene and increase its solubility in aqueous phase. Moreover, the solubilized 1-decene could more readily react with the rhodium catalyst on the surface of the micelle. Therefore, the hydroformylation reaction rates could be substantially accelerated by using the amphiphilic phosphine ligand when its concentration reaches its CMC. The lower conversion rate at the lower P/Rh ratio is ascribed to the lower DMOPPS concentration, which is lower than its CMC. On the contrary, exceedingly high DMOPPS to rhodium ratio resulted in a very low conversion rate, which is attributed to the formation of catalytic inactive complex [25]. A high DMOPPS concentration will shift the equilibrium to the left side and a coordination saturated rhodium complex $HRh(CO)(DMOPPS)_3$ would form (Scheme 1).

3.3. Catalyst recycles

The catalytic recycle experiments were conducted in four consecutive runs with the DMOPPS/Rh (molar ratio) at 4 (Table 2). The conversion rate of 1-decene was 93.6% in the first run and decreased to 70.9% in the second run, although the rhodium leaching into organic phase was very low according to the test by ICP-AES. It is possible that the oxidization of DMOPPS during the reaction or the



Scheme 1. Equilibrium of catalytic species in the hydroformylation process.



Scheme 2. Sketch map of 1-decene solubilized in DMOPPS micelle.

loss of DMOPPS during the sample handling results in the abatement of the conversion rates during the recycles. The fact that the conversion rate rose again after the addition of 2.0 mg of fresh phosphine in the fourth run might confirm the explanation.

3.4. Effect of the carbon chain length of olefins

The data in Table 3 clearly displayed the effects of the olefin carbon chain length on the Rh-DMOPPS catalytic performance in the aqueous biphasic hydrformylation of higher olefins. The molar ratio of DMOPPS to rhodium was 6 and the other reaction conditions were the same as in Fig. 2. When the reaction proceeded for 2 h, the conversions of the 1-octene, 1-decene, 1-dodecene, 1-tetradecene, and 1-hexadecene were 92.6%, 93.4%, 77.2%, 27.1%, and 22.8%, respectively. The conversions gradually dropped with the increase in olefin carbon chain length. 1-Octene or 1-decene that has the shorter carbon chain than DMOPPS does exhibited a higher hydroformylation activity. On the other hand, 1-tetradecene or 1-hexadecene having longer carbon chain exhibited a much lower reaction activity. These results again corroborated the matching effect between the carbon chain length of DMOPPS and that of olefins [26]. The olefin with proper carbon chain length could be readily solubilized into the hydrophobic micellar core that formed from the amphiphilic DMOPPS. On the contrary, the olefin with an alkyl chain that is too long is difficult to be incorporated into the micelle. However, if the reaction time was significantly prolonged, much higher conversions for both the 1-tetradecene and

Table 2
Catalysis recycle tests[a]

Run	Con. (%)	$S_{ald.}$ (%)	S_{iso} (%)	S_{alk} (%)	L/B	TOF (h^{-1})	Rh/ppm[b]
1	93.6	70.9	21.0	8.1	2.3	622.1	0.021
2	70.9	70.2	21.3	8.5	2.1	466.6	0.011
3	71.9	74.2	18.5	7.3	2.3	500.1	0.120
4[c]	92.2	83.2	12.0	4.8	2.3	719.2	0.091
5	80.6	66.7	24.1	9.2	2.3	504.0	0.102

[a] The molar ratio of DMOPPS to Rhodium is 4, stirring rate is 600 rpm and the other reaction conditions are the same as in Fig. 2.
[b] Rhodium content in organic phase.
[c] Addition of 2.0 mg of fresh DMOPPS.

Table 3
Effects of olefin chain length[a]

Olefin (time, h)	Con. (%)	$S_{ald.}$ (%)	S_{iso} (%)	S_{alk} (%)	L/B	TOF (h^{-1})
1-Octene (2)	92.6	77.6	16.6	5.8	2.4	673.7
1-Decene (2)	93.4	74.5	18.4	7.1	2.2	652.3
1-Doecene (2)	77.2	86.7	8.7	4.6	2.5	627.5
1-Tetradecene (2)	27.1	70.8	15.9	13.3	2.6	179.9
Hexadecane (2)	22.8	58.3	29.4	12.3	2.6	124.6
1-Tetradecene (7 h)	60.4	77.8	15.4	6.8	2.5	125.9
1-Tetradecene (22 h)	97.1	83.9	12.0	4.1	2.6	69.4
1-Hexadecane (7 h)	43.7	85.4	14.6	–	2.4	99.9
1-Hexadecane (22 h)	97.5	84.6	11.6	3.8	2.3	70.3

[a] *Reaction conditions*: n(DMOPPTS)/n(Rh) = 6. The other reaction conditions are the same as in Fig. 2.

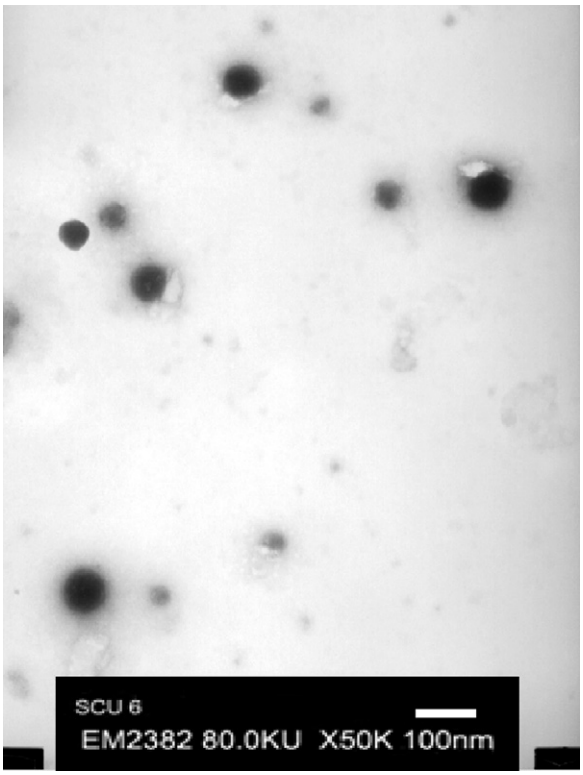
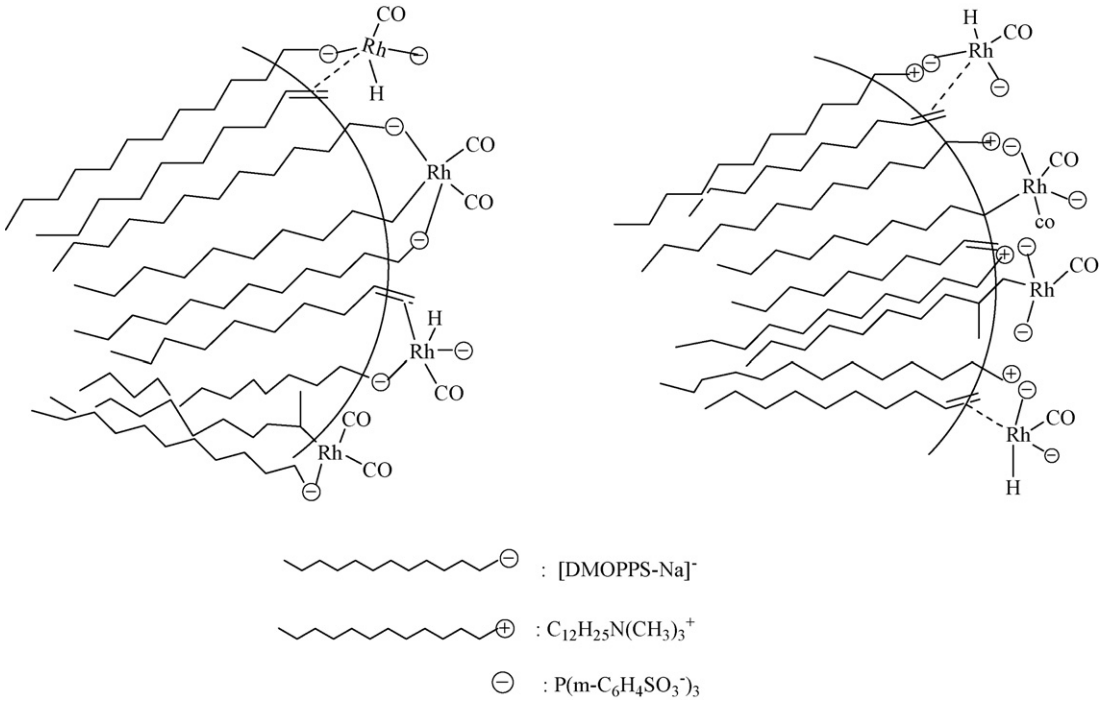


Fig. 3. TEM image of DMOPPS aqueous solution containing $RhCl(CO)(TPPTS)_2$ [DMOPPS]/[Rh] = 4, $[RhCl(CO)(TPPTS)_2]$ = 0.96 mmol/L.

the 1-hexadecene were achieved when the amphiphilic ligand, DMOPPS, was used with $RhCl(CO)(TPPTS)_2$ as the catalyst precursor. For example, when the reaction time was extended to 22 h, both the two long-chain olefins were almost completely converted. However, when the traditional non-amphiphilic ligand, TPPTS was used (also with $RhCl(CO)(TPPTS)_2$ as the catalyst precursor), the hydroformylation of 1-tetradecene and 1-hexadecene exhibited negligible conversion, even after the reaction time was extended to 48 h. This result clearly confirms the favorable catalytic performance by using the new amphiphilic DMOPPS ligand. As a matter of fact, in the aqueous biphasic catalysis system, this amphiphilic ligand may function not only as a phosphine ligand to stabilize the rhodium catalyst, but also as a micelle-forming agent. This micelle-forming property plays a significant role in enhancing the hydroformylation reaction rates of long chain olefins.

3.5. Comparison of Rh-DMOPPS and Rh-DTAI-TPPTS system

As discussed in the preceding section, the modification ligand, DMOPPS endows a surface-active property to the rhodium complex in the Rh-DMOPPS system. The amphiphilic ligand may aggregate to form an anionic micelle exposing the rhodium center at the micelle surface. This micelle-forming property is instrumental in enhancing the contacting opportunity between the rhodium catalyst and the olefin that is solubilized in the micelle. Therefore the reaction could be enormously accelerated. This mechanism of accelerating the reaction rate using amphiphilic ligand is similar to that using cationic surfactant, which has been thoroughly investigated in our previous reports [11,12,14]. However, there still exist some differences between them. In the former system, the rhodium catalytic active species is fixed and concentrated at the micellar surface via its coordination with the P atom, whereas in the latter case, the rhodium species is enriched only by an electrostatic interaction between the cationic end of the surfactant and the anionic catalytic active species, $[HRh(CO)m[P(m\text{-}C_6H_4SO_3^-)]n$ (m = 1, 2; n = 1, 2, 3) (Scheme 3). For a comparison of the catalytic performance, the hydroformylation of 1-decene catalyzed by $[RhCl(CO)(TPPTS)_2]$-TPPTS-DTAI (DTAI: $C_{12}H_{25}N(CH_3)_3I$) system was performed under the identical conditions when the $[RhCl(CO)(TPPTS)_2]$–DMOPPS system was used without the addition of any surfactant. The surfactant, n-$C_{12}H_{25}N(CH_3)_3I$, was elected and used as a catalysis

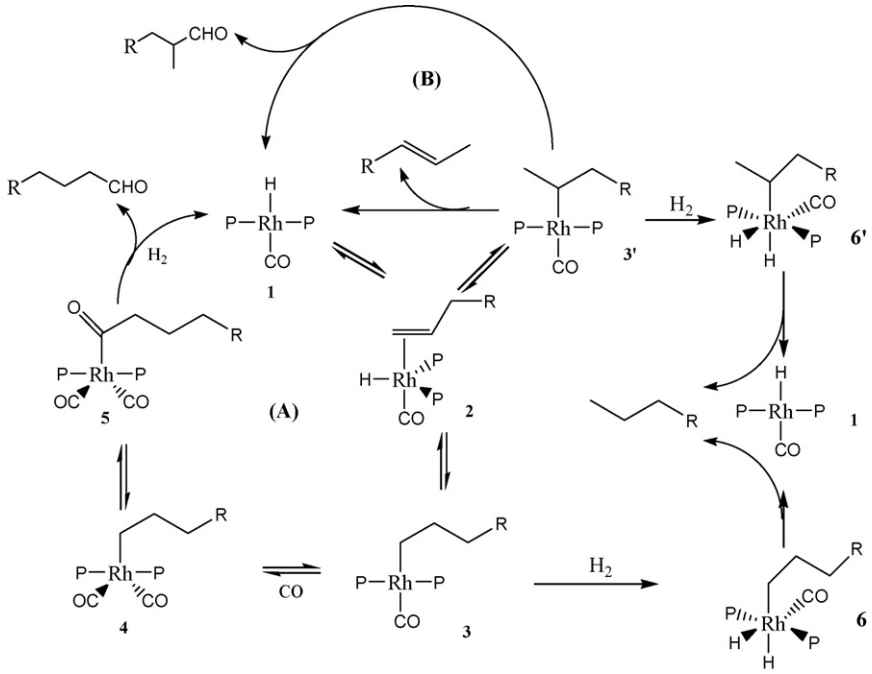


Scheme 3. Sketch maps of the catalytic-active species on the surface of the micelle (*Left*: Rh-DMOPPS system; *Right*: Rh-TPPTS-DTAI system).

Table 4
Comparison of catalytic performances between Rh-DMOPPS and Rh-TPPTS-DTAI system[a]

Catalysis system	Con. (%)	$S_{ald.}$ (%)	S_{iso} (%)	S_{alk} (%)	L/B	TOF (h^{-1})	Color of organic phase
Rh-DMOPPTS							
DMOPPTS/Rh = 2/1	51.7	41.9	41.5	16.6	1.5	203.1	Colorless
DMOPPTS/Rh = 4/1	93.6	70.9	21.0	8.1	2.3	622.1	Colorless
DMOPPTS/Rh = 8/1	63.4	91.3	6.1	2.6	2.5	542.7	Colorless
Rh-TPPTS-DTAI							
TPPTS/DTAI/Rh = 2/2/1	63.0	11.7	63.3	25.0	2.5	69.1	Yellow
TPPTS/DTAI/Rh = 4/4/1	66.1	14.4	60.2	25.4	2.4	89.2	Yellow
TPPTS/DTAI/Rh = 8/8/1	62.6	93.7	4.3	2.0	2.6	549.9	Light yellow

[a] Reaction conditions are the same as in Fig. 2.



Scheme 4. Mechanism of olefin hydroformylation catalyzed by the phosphine-modified rhodium complex.

promotion agent because it possesses an equal carbon chain length to that of DMOPPS. The results exhibited distinct catalytic performances by using the two different ways to enrich catalyst in the two systems. For instance, at the lower molar ratio of phosphine to rhodium, the Rh-DMOPPS system showed much better reaction selectivity toward aldehyde than the Rh-TPPTS-DTAI system did. When the molar ratio of DMOPPS to rhodium was 4 in the Rh-DMOPPS system, the conversion rate of 1-decene and the chemoselectivity to aldehyde were 93.6% and 70.9%, respectively. However, in the Rh-TPPTS-DTAI system, they were only 66.1% and 14.4%, respectively (Table 4).

The different property in the basicity of the two ligands (TPPTS and DMOPPS) is also possibly responsible for the distinct catalytic performances. The well-known hydroformylation mechanism for the phosphine-modified catalyst is shown in Scheme 4. The catalytic-active species **1** coordinates with the olefin, and then forms the alkyl rhodium complex **3**. The coordination with a carbon monoxide followed by CO insertion affords the acryl complex **5**. Subsequently, the oxidative addition of H_2 and the reductive elimination form the linear aldehyde product. Similarly, the catalysis circle B produces the branched aldehyde. There are also some undesired reactions in the hydroformylation process. The β-H elimination of species **3′** produces the double bond isomerization by-product. And oxidative addition of **3** and **3′** with H_2 followed by reductive elimination yields the double bond hydrogenation by-product. According to this mechanism, the more basic the rhodium complex is, the more inclined it will be to coordinate with CO. The coordination of CO could affect the formation of the species **4** and **5**. When their formation rates and equilibrium concentrations are increased, the catalytic process will proceed following the catalysis circle A or B and therefore, more aldehyde will be generated. The electron-donating methoxy group makes the DMOPPS modified-rhodium complex more basic thus leads to higher aldehyde production selectivity. The rhodium-complexes modified by TPPTS, on the contrary, produce more double bond isomerization and hydrogenation by-products.

4. Conclusion

A new amphiphilic phosphine DMOPPS was synthesized and utilized in the aqueous biphasic catalytic hydroformylation of long chain olefins. The rhodium catalyst modified with DMOPPS exhibited a high catalysis activity due to the surface activity of the amphiphilic ligand. The matching effect between the carbon chain length of DMOPPS and that of the olefin was observed. The studies on the other surface-active properties such as CMC, aggregation number and adsorption and surface tension behavior of the amphiphilic phosphine are in progress now.

Acknowledgement

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