

1-Dodecene Hydroformylation Catalyzed by Water Soluble Rhodium Phosphine Complex in Two-Phase System[†]

LI, Yao-Zhong(黎耀忠) CHEN, Hua(陈华) CHEN, Jun-Ru(陈骏如)
CHENG, Pu-Ming(程溥明) HU, Jia-Yuan(胡家元) LI, Xian-Jun*(李贤均)
Department of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

1-Dodecene hydroformylation catalyzed by water soluble rhodium complex $[\text{RhCl}(\text{CO})(\text{TPPTS})_2]$ was studied in the presence of TPPTS $[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3]$ and CTAB (cetyltrimethyl ammonium). The influence of reaction parameters was discussed in detail based on micelle effect in biphasic system. The modification for the microcircumstance of micelle interface was conducted by the introduction of a catalyst promoter TPPDS $[\text{PhP}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_2]$ into the reaction solution. A synergistic effect between TPPDS and TPPTS on the regioselectivity of 1-dodecene hydroformylation was observed. The selectivity of linear aldehyde in the products was so high as 95.7% at the molar ratio of $[\text{TPPDS}]/[\text{TPPTS}] = 0.5$.

Keywords Hydroformylation, water soluble rhodium complex, 1-dodecene, two-phase catalytic system

Introduction

Homogeneous catalysis provides a mild and selective synthesis route of valuable chemicals. However, the separation of organic products from catalyst is trouble and even difficult. Aqueous/organic two-phase catalysis simplifies the separation process by decantation and facilitates catalyst recycling. Therefore, the study of two-phase catalytic system has attracted great attention in recent years and some new two-phase catalytic processes using water soluble transition metal complexes with ligand TPPTS $[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3]$ and TPPMS $[\text{Ph}_2\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})]$ have been successfully developed and applied to industrial productions.^{1,2} Nevertheless, the

reaction rate could be reduced to such an extent that it becomes unacceptable when the solubility of the substrates in aqueous phase is too low, *e. g.* in long-chain olefin hydroformylation. A lot of efforts have been done for improving the affinities between the two phases. The addition of co-solvents,³ surfactants,⁴⁻⁶ co-ligand Ph_3P ^{7,8} and modified cyclodextrins,^{9,10} into biphasic system can efficiently increase the hydroformylation rate. Recently, many diphosphine ligands with surfactant group, such as the sulfophenylalkyl derivatives of BISBI and BINAP,^{11,12} as well as Xantphos,¹³ have been studied in long-chain olefin hydroformylation. Although these rhodium diphosphine complexes exhibit better activity and high regioselectivity, the water soluble diphosphine ligand are very expensive. Among above-mentioned approaches the Rh-TPPTS system adding cationic surfactant, such as cetyltrimethyl ammonium bromide (CTAB), is the most cheap and prospective, but the regioselectivity of the catalyst system was low. A combinatorial system with high activity and high regioselectivity in long-chain olefin hydroformylation can be designed if the behaviors of cationic surfactant micelle in two-phase catalytic system are deeply understood. In this paper we report the performance of the catalyst system $\text{RhCl}(\text{CO})(\text{TPPTS})_2\text{-TPPTS-CTAB}$ and novel high regioselective catalyst system, which consisted of $\text{RhCl}(\text{CO})(\text{TPPTS})_2\text{-TPPTS-CTAB}$ and a promoter TPPDS $[\text{PhP}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_2]$, in aqueous/organic two-phase

* E-mail: scuulixj@mail.sc.cninfo.net

Received April 24, 2000; accepted October 31, 2000.

[†]Special paper from the "China-Netherlands Bilateral Symposium on Organometallic Chemistry and Catalysis", Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China, 1999.

Project supported by the National Natural Science Foundation of China and the SINOPEC (No. 29792074).

reaction of 1-dodecene hydroformylation.

Experimental

Materials

All organic solvents and cationic surfactant cetyltrimethyl ammonium bromide (CTAB) were analytical reagents. 1-Dodecene (Fluka 96%) was commercial and not treated further. TPPTS [$P(m-C_6H_4SO_3Na)_3$], TPPDS [$PhP(m-C_6H_4SO_3Na)_2$] and rhodium complex $RhCl(CO)(TPPTS)_2$ were prepared by the method described in the literature.^{14,15} The oxide content in TPPTS and TPPDS was less than 5%. Water was doubly distilled. Hydrogen (99.99%) and carbon monoxide (99%) were mixed with the ratio of 1:1 and treated with deoxidizer and desulfurizer prior to use.

Hydroformylation of 1-dodecene

Hydroformylation of 1-dodecene was conducted in a stainless steel autoclave of 100 mL with a magnetic stirrer. After rhodium complex $RhCl(CO)(TPPTS)_2$, TPPTS, TPPDS, CTAB, 1-dodecene and water were added to autoclave, the reactor was evacuated and purged with syngas for three times. The reaction solution was heated at desired temperature and then syngas was introduced. The reaction was carried out under a constant pressure for a given time. The products in organic phase were analyzed by GC HP1890 II equipped with FID and a capillary column (30 m \times 0.25 mm) SE-30.

Results and discussion

Effect of total and partial pressure

The effects of syngas total pressure and partial pressure of H_2 and CO on 1-dodecene hydroformylation were summarized in Fig. 1 and Table 1. The results in Fig. 1 showed that when the total pressure was lower than 0.5 MPa, the reaction rate increased with increasing syngas pressure, but the rate almost did not change over 0.5 MPa. The ratios of linear/branched aldehyde (L/B value) in the products decreased with the increase of syngas pressure. The data in Table 1 indicated that when the total pressure was maintained constant (0.5 MPa) the increase of partial pressure of hydrogen promoted the re-

action and the formation of linear aldehyde. The L/B values were 21.6 and 26.6 as the ratios of partial pressure between H_2 and CO were 2:1 and 4:1, respectively. It suggested that the higher partial pressure of hydrogen was favourable for the formation of linear aldehyde, but this would cause the hydrogenation of 1-dodecene. The excessive high partial pressure of carbon monoxide would reduce the reaction rate.

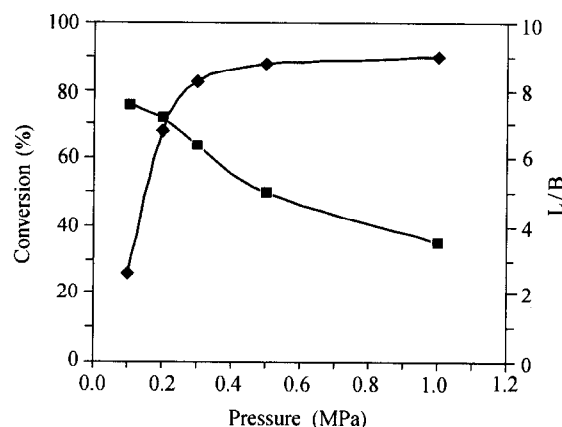


Fig. 1 Effect of total pressure on 1-dodecene hydroformylation. Reaction conditions; $[Rh] = 1.86 \times 10^{-3}$ mol/L, $[TPPTS]/[Rh] = 16$, $[CTAB] = 1.1 \times 10^{-2}$ mol/L, 1-dodecene: 22.6 mmol, cyclohexane: 5 mL, $CO/H_2 = 1:1$, $100^\circ C$, 120 min. The total pressures are constant during the reaction, \blacklozenge : conversion, \blacksquare : L/B—linear/branched aldehyde ratio.

Table 1 Effect of partial pressure of CO and H_2 on the hydroformylation

$CO:H_2:Ar$ (pressure ratio)	Conc. (%)	L/B	<i>n</i> -Dodecane (%)
4:1:0*	60.4	4.7	/
2:1:2	74.1	5.9	/
1:1:3	75.6	10.1	/
1:2:2	77.0	21.6	5.98
1:4:0	79.1	26.6	5.91

Reaction conditions; $[Rh] = 9.6 \times 10^{-4}$ mol/L, $[TPPTS]/[Rh] = 16$, 1-dodecene: 22.6 mmol, cyclohexane: 5 mL, total pressure = 0.5 MPa, $80^\circ C$, $t = 150$ min, * $t = 180$ min.

Effect of temperature

The effects of temperature on 1-dodecene hydroformylation were determined at two different molar ratios of $[TPPTS]/[Rh]$ (15 and 30) and the constant pressure (1 MPa). The reaction rate constants and L/B value

at different temperature were given in Table 2. The ratio of linear/branched aldehyde decreased with increasing the reaction temperature and decreasing the ratio of $[\text{TPPTS}]/[\text{Rh}]$. The activation energies of 1-dodecene hydroformylation in two-phase catalytic reaction conditions were 71.4 and 82.5 kJ/mol at $[\text{TPPTS}]/[\text{Rh}] = 15$ and $[\text{TPPTS}]/[\text{Rh}] = 30$, respectively. The higher activation energies in two-phase catalytic system than in homogeneous reaction (57.1 kJ/mol)¹⁶ were in agree-

ment with the higher dissociation energy of TPPTS from $\text{HRh}(\text{CO})(\text{TPPTS})_3$ than that of PPh_3 from $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.¹⁷ The data showed that the diffusion factor of the reactants across the phase boundary had been eliminated at the stirring rate of 600 rpm.¹⁸ The increase of $[\text{TPPTS}]/[\text{Rh}]$ ratio was not favourable for the dissociation of TPPTS from $\text{HRh}(\text{CO})(\text{TPPTS})_3$, which would make the increase of activation energy at higher $[\text{TPPTS}]/[\text{Rh}]$ ratio.

Table 2 Effect of reaction temperature on the rate constant k of 1-dodecene hydroformylation in two-phase system

$[\text{TPPTS}]/[\text{Rh}]$	30				15				
	T (K)	343	353	363	373	343	353	363	373
$k \times 10^{-3}$ (min^{-1})		1.61	4.33	8.28	15.35	2.61	6.03	9.69	19.13
r^2 *		0.995	0.999	0.998	0.995	0.998	0.997	0.998	0.998
L/B		5.1	5.5	4.1	4.3	3.8	3.7	3.4	3.6

Reaction conditions; 1.0 MPa (constant), $[\text{Rh}] = 9.6 \times 10^{-4}$ mol/L, $\text{CO}:\text{H}_2 = 1:1$, stirring rate; 600 rpm, * Correlation coefficient.

Effect of $[\text{TPPTS}]/[\text{Rh}]$ ratio

When the molar ratio of $[\text{TPPTS}]/[\text{Rh}]$ was lower than 20, the conversion of 1-dodecene increased with increasing $[\text{TPPTS}]/[\text{Rh}]$ ratio, but it decreased as the molar ratio of $[\text{TPPTS}]/[\text{Rh}]$ was over 25, see Fig 2. The ratio of linear/branched aldehyde always increased with raising the molar ratio of $[\text{TPPTS}]/[\text{Rh}]$. The increase of $[\text{TPPTS}]/[\text{Rh}]$ ratio under lower TPPTS concentration could be beneficial for the formation and stabilization of catalytic active species with following equi-

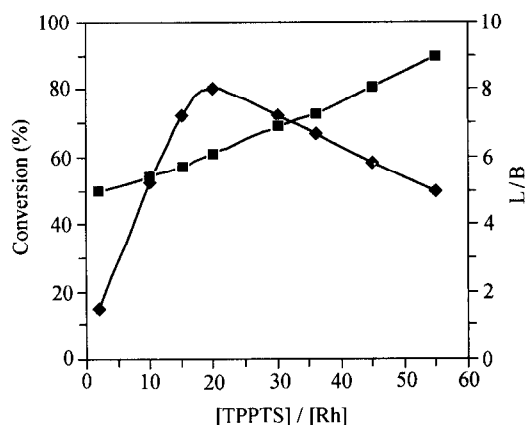
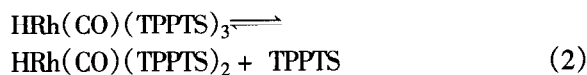
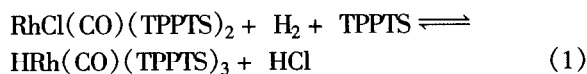


Fig. 2 Effect of molar ratio of TPPTS to rhodium complex on 1-dodecene hydroformylation. Reaction conditions: $[\text{Rh}] = 9.6 \times 10^{-4}$ mol/L, total pressure = 0.5 MPa, the other conditions are the same as in Fig. 1, \blacklozenge : conversion, \blacksquare : L/B.

brium and thus the reaction rate increased with raising $[\text{TPPTS}]/[\text{Rh}]$ ratio.



The too high ratio of $[\text{TPPTS}]/[\text{Rh}]$ would inhibited olefin coordination because the competition coordination of TPPTS with rhodium atom was stronger than that of olefin, thereby the dissociation of TPPTS from $\text{HRh}(\text{CO})(\text{TPPTS})_3$ forming coordination unsaturated catalytic active species $\text{HRh}(\text{CO})(\text{TPPTS})_2$ became difficult. This was agreement with the above-mentioned data of activation energy.

Effect of pH value

The effect of pH values of aqueous solution on the catalytic activities was graphically showed in Fig. 3. The curves a and b displayed the similar variation tendency although the reaction pressures were different. The results indicated that the highest activity exhibited at about $\text{pH} = 6-8$, *i. e.* the aqueous solution was near neutrality, and the activity would decrease whether the aqueous solution was of acidity or basicity. This was ascribed to that the increase of acidity in aqueous solution

would be unfavourable for the formation of catalytic active species $\text{HRh}(\text{CO})(\text{TPPTS})_2$ as showed in above mentioned Eqs. (1) and (2). Wilkinson *et al.*¹⁹ reported the similar equilibrium movement in homogeneous catalysis with an analogue $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ as catalyst. A longer induction period for 1-dodecene hydroformylation in the acidic solution was observed. If the acidity was such strong as $\text{pH} = 2.5$, the reaction was almost inhibited at 0.5 MPa (curve a). The reaction did not also occur under $\text{pH} = 4.5$ and atmospheric pressure (curve b). The surfactant CTAB could decompose in basic solution and a slurry material formed after end of the reaction. Probably this was the main factor of the conversion drop in the basic solution.

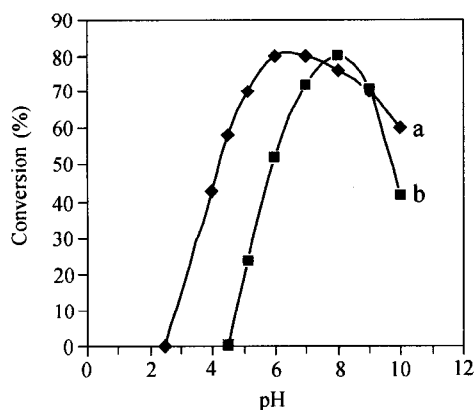


Fig. 3 Effect of aqueous pH value on 1-dodecene hydroformylation. Reaction conditions: 1-dodecene; 45 mmol, H_2O ; 40 mL, 80°C , 8 h, the others are the same as in Fig. 1, ◆; 0.5 MPa, ■; atmospheric pressure.

Effect of catalyst and 1-dodecene concentration

When the amount of $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ and 1-dodecene, as well as the ratio of $[\text{TPPTS}]/[\text{Rh}]$ were maintained constant, the change of water and organic phase volume would influence the hydroformylation. The results were listed in Table 3. The fact that the conversion increased with increasing aqueous volume could be due to the extension of the interfacial area between two phases. Although the catalyst concentration in aqueous phase was diluted by the addition of water, the rhodium complex concentration enriched in interfacial layer between two phases could not change obviously.¹⁸ The increase of organic solvent would cause the dilution of substrate and then 1-dodecene conversion decreased.

Table 3 Effect of volume ratio of H_2O to organic solvent on the hydroformylation

H_2O (mL)	Cyclohexane (mL)	Conv. (%)	L/B	TOF (min^{-1})
10	5	75.1	7.1	10.1
20	5	86.7	5.5	11.8
30	5	89.9	6.0	12.0
20	10	84.4	5.3	11.5
20	20	66.6	5.6	9.1

Reaction conditions: $[\text{Rh}] = 1.38 \times 10^{-3}$ mol/L, $[\text{TPPTS}]/[\text{Rh}] = 28$, 1-dodecene; 22.6 mmol, 100°C , 0.5 MPa.

When the volume of organic and aqueous phase were kept constant, the reaction rate increased with increasing 1-dodecene concentration in the range of 0.5—3.5 mol/L, see Fig 4. The range of 1-dodecene concentration in two-phase system was much higher than that in homogeneous catalysis using Wilkinson catalyst. In the latter case, the rate did not change as the olefin concentration was over 0.36 mol/L.¹⁶ This difference exhibited the characteristics of micelle catalysis in aqueous/organic two-phase system wherein olefin hydroformylation occurred in interfacial layer rather than in organic phase. The solubilization of olefin in micelle created an efficient transfer passway of olefin from micellar core to its interface. If olefin solubilization was not saturated as olefin concentration was lower than 3.5 mol/L, olefin solubilization would increase with increasing its concentration (as showed in Fig 4). This would be favourable for raising the reaction rate. When olefin solubilization was

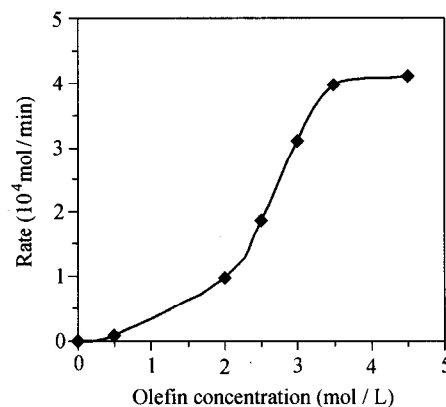


Fig. 4 Effect of olefin concentration on reaction rate of 1-dodecene hydroformylation. Reaction conditions; the volume of organic phase was kept constant (15 mL), $[\text{Rh}] = 9.7 \times 10^{-4}$ mol/L, $[\text{CTAB}] = 1.37 \times 10^{-2}$ mol/L, 80°C , 0.5 MPa.

saturated in a certain CTAB concentration, the further increase of olefin concentration would not influence the reaction rate as observed over 3.5 mol/L of its concentration.

High regioselectivity catalyst system of 1-dodecene hydroformylation

The above mentioned and reported results²⁰ demonstrated that the micelle formation played very important role for the acceleration of biphasic catalytic reaction, but the ratio of linear/branched aldehyde in the products was low. In order to promote the formation of linear aldehyde, we studied the modification of the microcircumstance of catalytic reaction. TPPDS as a promoter was introduced into the biphasic system. The data listed in Fig. 5 showed that the addition of TPPDS could remarkably improve the regioselectivity of 1-dodecene hydroformylation and greatly increase the ratio of linear/branched aldehyde in the products. When the molar ratio of total phosphine/rhodium complex concentration was kept constant and the phosphine ligand TPPTS or TPPDS was used alone, the ratio of linear/branched aldehyde was low. However, when TPPTS and TPPDS were simultaneously used, a synergistic effect promoting the formation of linear aldehyde was observed. The ratio of linear/branched aldehyde increased rapidly with the addition of TPPDS into the catalytic system when the molar ratio between TPPDS and TPPTS was lower than 0.5. The regioselectivity was so high as 95% at $[\text{TPPDS}]/[\text{TPPTS}] = 0.5$ (molar ratio), which could be compared with the results reported in Ref. 11 using very expensive diphosphine ligand. The ratio of $[\text{TPPDS}]/[\text{TPPTS}]$ increased further, the regioselectivity decreased gradually. The change of $[\text{TPPDS}]/[\text{TPPTS}]$ ratio did not obviously influence the catalytic activity. The results suggested that the addition of TPPDS caused a subtle variation of the catalytic active species. When a part of TPPTS in rhodium complex was displaced by TPPDS, a new rhodium complex $\text{HRh}(\text{CO})(\text{TPPTS})_m(\text{TPPDS})_n$ could form. Its steric effect and d orbital electron density of rhodium atom would be different from the analogues containing only TPPTS or TPPDS as ligand. The gentle modification for rhodium catalyst created a favourable microcircumstance in Stern layer of micelle for the formation of linear aldehyde in long chain olefin hydroformylation.

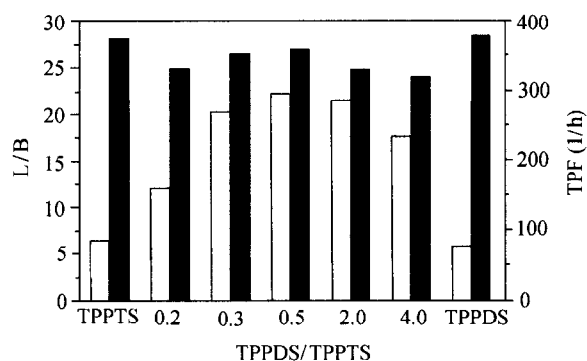


Fig. 5 Effect of molar ratio of TPPDS to TPPTS on 1-dodecene hydroformylation. Reaction conditions: $[\text{Rh}] = 1.0 \times 10^{-3}$ mol/L, $[\text{CTAB}] = 5.53 \times 10^{-3}$ mol/L, 1-dodecene: 13.5 mmol, H_2O : 15 mL, 100°C , 1.5 MPa (constant), \square : L/B, \blacksquare : TPF.

Reference

- Cornils, B. *J. Mol. Catal., A: Chemical* **1999**, *143*, 1.
- Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177.
- Purwanto, P.; Delmas, H. *Catal. Today* **1995**, *24*, 135.
- Chen, H.; Li, Y. Z.; Chen, J. R.; Cheng, P. M.; He, Y. E.; Li, X. J. *J. Mol. Catal. A: Chemical* **1999**, *149*, 1.
- Russel, M. J. H. *Platinum Metals Rev.* **1998**, *32*, 179.
- Vyve, F. V.; Renken A. *Catal. Today* **1999**, *48*, 237.
- Chaudhai, R. V.; Bhanage, B. M.; Dashpande, H. R. M.; Delmas, H. *Nature* **1995**, *373*, 501.
- Kalck, P.; Miquel, L.; Dessoudeix, M. *Catal. Today* **1998**, *42*, 431.
- Monflier, E.; Tilloy, S.; Fremy, G.; Gastanet, Y.; Montreux, A. *Tetrahedron Lett.* **1995**, *52*, 9481.
- Tilloy, S.; Bertoux, F.; Montreux, A.; Monflier, E. *Catal. Today* **1999**, *48*, 245.
- Hanson, B. E.; Ding, H.; Kohlpaintner, C. W. *Catal. Today* **1998**, *42*, 421.
- Ding, H.; Hanson, B. E.; Bakos, J. *Angew. Chem.* **1998**, *107*, 1728.
- Goedheijt, M. S.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M. *J. Mol. Catal. A: Chemical* **1998**, *134*, 243.
- Chen, H.; Li, X. J.; Li, Y. Z.; Liu, H. C. *CN. 96120055*, **1996**, 3.
- Chen, H.; Li, Y. Z.; Li, X. J.; Cheng, P. M. *CN 99106168*, **1999**, 3.
- Harvath, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. J. *Catal. Lett.* **1998**, *2*, 85.
- Chen, H. *Ph. D. Thesis*, Sichuan University, Chengdu, **1999**.
- Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 3133.
- Chen, H.; Li, Y. Z.; Cheng, P. M.; Chen, J. R.; Hu, J. Y.; Li, X. J. *Chinese J. Catal.* **1999**, *20*, 571.

(E200004095 JIANG, X.H.; DONG, L.J.)