Novel effect of additional metal ion on hydroformylation of hexene-1 in biphasic system

Yulin Huang [a,b,*], Li-e Min [c], Yaozhong Li [a], Hua Chen [a],
Puming Cheng [a], Xianjun Li [a,1]

[a] *Department of Chemistry, Sichuan University, Chengdu 610064, China*
[b] *Catalysis IV, Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China*
[c] *Department of Biology, Sichuan University, Chengdu 610064, China*

Abstract

The hydroformylation of hexene-1 is carried out in the biphasic system with $RhCl(CO)(TPPTS)_2$ (TPPTS $= P(C_6H_4\text{-}m\text{-}SO_3 Na)_3$), TPPTS and CTAB (cetyltrimethylammonium bromide). The rhodium catalyst concentration in interface has a drastic effect on reaction rate, and additional salts make reaction rate decrease obviously because they influence the distribution of catalyst in the biphasic system. Inorganic salts also have influence on the turnover frequency in the order: $TOF(M^{3+}) < TOF(M^{2+}) < TOF(M^+)$ (M^{n+} is a metal cation with a charge of $+n$). However, additional inorganic salts do not change the regioselectivity obviously in this hydroformylation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Because of the easy separation and recycling of costly water-soluble organometallic catalysts from products, the development of aqueous/organic biphasic catalysis has been attracting increasing attention since 1973 [1–13]. In spite of success in the biphasic propene hydroformylation catalysis [14], the application of trisodium salt of tri(*m*-sulfonphenyl)-phosphine (TPPTS) and $HRh(CO)(TPPTS)_3$ to hydroformylation of higher olefins is still limited owing to the poor reaction rates. In order to improve the reaction rate of hydroformylation of higher olefins in the biphasic system, several methods are studied. One approach involves using amphiphilic additives or ligands, but further difficulties in catalyst recycling and product separation often occur [15–20]. Another approach involves adding quaternary ammonium or phosphonium salts that act as solubilizing agents in water [6,7,20–27]. In the presence of surfactants, such as CTAB (cetyltrimethylammonium bromide), water-soluble catalyst and ligand might show higher activity, better regioselectivity and much lower consumption in biphasic olefin hydroformylation [28,29]. In the first approach, Hanson and coworkers [17,30,31] have discovered that both size and charge of the added cation have strong influence on the

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* Corresponding author. Present address: Catalysis IV, Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China. Tel.: +86-21-6546-8017; fax: +86-21-6846-2283.
E-mail address: yulinhuangch@yahoo.com (Y. Huang).

[1] Co-corresponding author.

biphasic hydroformylation. On one hand, reaction activity and regioselectivity increase with the increase of ionic strength while a surfactive phosphine being capable of forming micelles is used in the biphasic hydroformylation system because the highly ionic strength can stabilize the complex HRh(CO)(TPPTS)$_3$ in water. On the other hand, the size and charge of cation also play important roles in determining the steric structure of catalytic intermediate that might contribute to the diverse influence on the regioselectivity of product. For example, the addition of cations such as Li$^+$, Na$^+$ and Cs$^+$ can improve the product regioselectivity compared with that without additional salt, but additional Al^{3+} is detrimental to the regioselectivity.

We have investigated the influence of a series of inorganic salts on the hydroformylation of hexane-1 catalyzed by RhCl(CO)(TPPTS)$_2$–TPPTS–CTAB in the biphasic catalytic system [32–34]. The results reveal that not only the ionic strength, the size and charge suggested by Hanson and coworkers in Refs. [17,30,31] but also solubilization promoted by introducing of inorganic salts greatly influences the conversion of hexene-1 hydroformylation in this biphasic catalysis. We have found these cations and anions make reaction rate drop with different degrees as follows: (1) Na$^+$ > K$^+$ ≈ Li$^+$ > Zn^{2+} > Mg^{2+} > Ca^{2+} ≫ Ni^{2+} > Fe^{2+} > Sr^{2+} > Cu^{2+} > Fe^{3+} > Al^{3+} > Cr^{3+}; (2) SO$_4$$^{2-}$ > H$_2$PO$_4$$^-$ > EDTA^{2-} > I$^-$ > HCO$_3$$^-$ > Br$^-$ > B$_4$O$_7$$^{2-}$ > Cl$^-$ > S$_2$O$_4$$^{2-}$ > S$_2$O$_3$$^{2-}$ > CO$_3$$^{2-}$ > SO$_3$$^{2-}$.

In this paper, it is reported at the first time that additional metal sulfates affect the biphasic hydroformylation rate of hexene-1 because catalyst concentration in interface has changed correspondingly. We believe this result would give some new and interesting information and ideas to the studies about the mechanism of the biphasic catalytic system catalyzed by RhCl(CO)(TPPTS)$_2$–TPPTS–CTAB.

2. Experimental

2.1. General

TPPTS was prepared by the reported method [25] and the procedure for preparing RhCl(CO)(TPPTS)$_2$ was described elsewhere [27]. H$_2$ (99.99% pure) and CO (99.99% pure) were purchased from Chengdu Institute of Organic Chemistry in Chinese Academy of Science and deoxygenated in prior. Distilled water was freshly redistilled using known procedures and degassed by argon before use. Hexene-1 (Sigma, ≥97.0% pure), methylcyclohexane (MCH, Acros, ≥99.9% pure), CTAB, Na$_2$SO$_4$, NiSO$_4$, FeSO$_4$, Fe$_2$(SO$_4$)$_3$, Cr$_2$(SO$_4$)$_2$ were obtained commercially as analytic grade and used without further purification.

2.2. Hydroformylation procedure

The reaction was carried out in a 100 ml stainless steel autoclave equipped with a pressure gauge, a magnetic stirrer and temperature controlled heating. All the reactions and manipulations were carried out under nitrogen or argon. In a typical hydroformylation reaction, an organic layer (5.0 ml MCH and 5.0 ml hexene-1) and an aqueous layer (30.0 ml solution with 0.354 mmol/l in RhCl(CO)(TPPTS)$_2$ and 10.62 mmol/l in TPPTS) were charged into the autoclave. Rhodium to hexene-1 ratio was 1:3800. Amounts of CTAB, Na$_2$SO$_4$ and other salts were adjusted on the necessary basis. The contents were flushed several times with argon followed by CO/H$_2$ (volume ratio, 1:1) and heated to the desired temperature under stirring. After attaining the temperature (90 °C), the autoclave was pressured with CO/H$_2$ to the desired level (1.5 MPa). To maintain a constant pressure in the reactor, CO/H$_2$ was fed through a constant pressure regulator. After reaction time (2 h), reaction was terminated by cooling the reactor in an ice-water bath. Then CO/H$_2$ was released.

2.3. Analysis and characterization

The analysis of liquid samples was carried out using a gas chromatograph (HP1890II) equipped with an SE-30 column (30 m × 0.25 mm × 0.1 μm) and a flame ionization detector (FID). The reaction activity and regioselectivity were expressed as the average turnover frequency and regioselectivity as follows:

$$\text{TOF (h}^{-1}) = \frac{\text{no. of moles of heptaldehyde}}{\text{no. of moles of rhodium catalyst} \times \text{time (h)}}$$

$$\text{Regioelectivity (\%)} = \frac{l}{l+b} \times 100\% = \frac{\text{no. of moles of linear-heptaldehyde}}{\text{no. of moles of linear- and branched-heptaldehydes}} \times 100\%$$

Then organic and water phases were separated after taking out the interface phase (2.0 ml, including 1.0 ml organic phase and 1.0 ml water phase just near their interface). The moles of rhodium catalysts in three parts (Rh_{org}, Rh_{aqu}, $Rh_{interface}$) were determined by ICP (Jarrel-Ash Division ICAP 900(N+M)). The percentage of rhodium in every part was calculated as:

$$\frac{Rh_{aqu}}{Rh_{total}} \text{(\%)} = \frac{Rh_{aqu}}{Rh_{aqu} + Rh_{interface} + Rh_{org}} \times 100\%$$

$$\frac{Rh_{interface}}{Rh_{total}} \text{(\%)} = \frac{Rh_{interface}}{Rh_{aqu} + Rh_{interface} + Rh_{org}} \times 100\%$$

$$\frac{Rh_{org}}{Rh_{total}} \text{(\%)} = \frac{Rh_{org}}{Rh_{aqu} + Rh_{interface} + Rh_{org}} \times 100\%$$

3. Results

3.1. Effect of CTAB on the hydroformylation

Effects of surfactants on the reaction rate of hydroformylation of olefins in the biphasic catalytic system were investigated carefully in literature [29]. CTAB was found to be the most suitable surfactant to increase reaction rate and regioselectivity of the hydroformylation catalyzed by $RhCl(CO)(TPPTS)_2$–TPPTS. Both hydroformylation activity and regioselectivity increased with increasing quantity of CTAB before their maximum values reached as shown in Table 1.

However, effect of CTAB on the distribution of catalyst in this biphasic system has not been investigated up to date. Effects of CTAB on TOF and the distribution of rhodium are also studied carefully. As listed in

Table 1, rhodium in interface ($Rh_{interface}$) is accumulated with the addition of CTAB, at the same time TOF also increases obviously, but rhodium in both water (Rh_{aqu}) and organic phase (Rh_{org}) decreases.

3.2. Effect of Na_2SO_4 on the hydroformylation

It is found that both hydroformylation rate and regioselectivity might change obviously with additional inorganic salts [32,33]. As shown in Table 2, with increasing concentration of Na_2SO_4, both TOF and $Rh_{interface}/Rh_{total}$ decrease. However, obviously percentage of rhodium catalyst in water phase (Rh_{aqu}/Rh_{total}) rises correspondingly. These results suggest that effects of Na_2SO_4 on TOF and $Rh_{interface}$ are consistent. The regioselectivity does not change obviously in this system although it is reported that inorganic salts have some effect on selectivity [17,30,31].

3.3. Effect of different inorganic salts on the hydroformylation

Recently, Hanson and coworkers [17,30,31] and our group [32,33] have investigated the effect of inorganic salts on the biphasic catalytic system. In order to find a rule about the effect of different cations on this biphasic hydroformylation, effects of Na_2SO_4, $NiSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$ and $Cr_2(SO_4)_3$ on TOF and regioselectivity are studied and listed in Table 3. With equal concentration of cations, effects of these inorganic salts are in the order: $TOF(M^{3+}) < TOF(M^{2+}) < TOF(M^+)$. The same order is also obtained for the

Table 1
Effect of CTAB on the distribution of rhodium and TOF[a]

Entry	CTAB ($\times 10^{-4}$ mol/l)	Rh_{aqu}/Rh_{total} (%)	$Rh_{interface}/Rh_{total}$ (%)	Rh_{org}/Rh_{total} (%)	TOF (h^{-1})	$l/(l+b)$ (%)
1	0	>99.5	0.4	<0.1	146	54.5
2	4.6	91.1	4.2	4.7	538	80.0
3	9.20	78.0	8.5	13.5	838	80.8
4	11.4	71.9	27.9	0.2	970	81.1
5	15.0	71.4	28.2	0.4	970	81.1

[a] Reaction conditions: [Rh], 3.54×10^{-4} mol/l; [hexene-1], 4.0 mol/l; [MCH], 3.92 mol/l; V_{H_2O}:$V_{(MCH+hexene-1)}$ = 3:1; [TPPTS]:[Rh], 30:1; V_{H_2}:V_{CO} = 1:1, temperature, 90 °C; P = 1.5 MPa; reaction time, 2 h.

Table 2
Effect of Na_2SO_4 on the distribution of rhodium and TOF[a]

Entry	Na_2SO_4 $(\times 10^{-1}$ mol/l)	Rh_{aqu}/Rh_{total} (%)	$Rh_{interface}/Rh_{total}$ (%)	Rh_{org}/Rh_{total} (%)	TOF (h^{-1})	$l/(l+b)$ (%)
1	0	71.9	27.9	0.2	970	81.1
2	2.0	80.2	19.6	0.2	935	81.5
3	8.0	88.9	10.8	0.3	870	81.5
4	16.0	93.6	6.1	0.3	755	81.8

[a] Reaction conditions are the same as in Table 1 except [CTAB] $= 1.14 \times 10^{-3}$ mol/l.

Table 3
Effect of different salts on the distribution of rhodium and TOF (other conditions are the same as in Table 2)

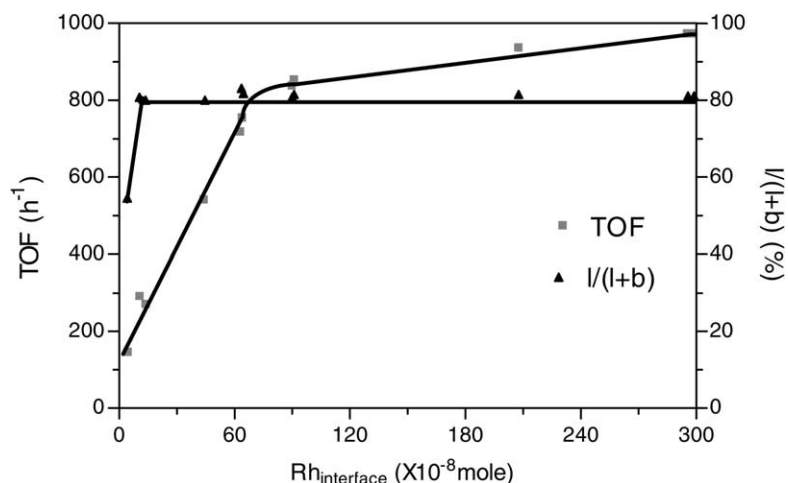| Entry	$M_x(SO_4)_y$[a]	Rh_{aqu}/Rh_{total} (%)	$Rh_{interface}/Rh_{total}$ (%)	Rh_{org}/Rh_{total} (%)	TOF (h^{-1})	$l/(l+b)$ (%)
1	Na_2SO_4	71.9	27.9	0.2	970	81.8
2	$NiSO_4$	88.2	8.6	3.2	850	81.5
3	$FeSO_4$	91.9	6.0	2.1	718	83.1
4	$Fe_2(SO_4)_3$	98.7	1.0	0.3	291	80.0
5	$Cr_2(SO_4)_3$	98.5	1.3	0.2	269	80.8

[a] $[M^{n+}] = 1.78 \times 10^{-3}$ mol/l.

Fig. 1. The effect of $Rh_{interface}$ on TOF and regioselectivity.

change in $Rh_{interface}/Rh_{total}$. The regioselectivity also hardly changes as a whole except that the addition of $FeSO_4$ is favorable for regioselectivity but $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ are unfavorable.

3.4. Effect of $Rh_{interface}$ on the hydroformylation

As shown in Fig. 1, the increase in $Rh_{interface}$ results in increase in TOF. TOF leveled off at $970\,h^{-1}$ when $Rh_{interface}$ is about 1.2×10^{-6} mol. With further accumulation of $Rh_{interface}$, TOF scarcely changes. However, regioselectivity does not change obviously except that the regioselectivity without added CTAB is very low.

4. Discussion

In this biphasic hydroformylation of hexene-1, mass transfer velocity between water and organic phases is a very important limiting factor to the reaction activity. It is well known that $RhCl(CO)(TPPTS)_2$ could
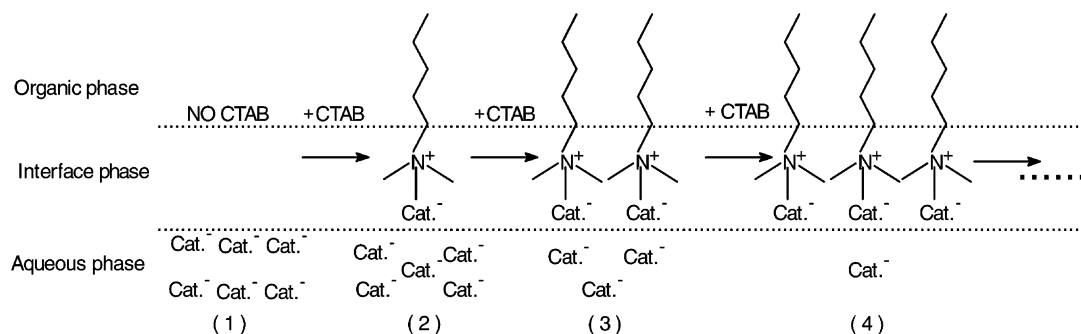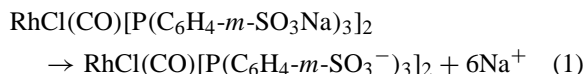
Fig. 2. A possible mode of the interaction between CTAB cations and catalyst anions [Cat.$^-$: RhCl(CO)[P(C$_6$H$_4$-m-SO$_3$$^-$)$_3$]$_2$].

dissociate easily as follows:

RhCl(CO)[P(C$_6$H$_4$-m-SO$_3$Na)$_3$]$_2$

$$\rightarrow \text{RhCl(CO)[P(C}_6\text{H}_4\text{-}m\text{-SO}_3{}^-)_3]_2 + 6\text{Na}^+ \quad (1)$$

The hexavalent anion, RhCl(CO)[P(C$_6$H$_4$-m-SO$_3$$^-$)$_3$]$_2$, would disperse almost homogeneously in the water phase. In contrast, the reactant hexene-1 would dissolve homogeneously in organic phase. So coordination of hexene-1 with rhodium, which is the key step in the hydroformylation cycle, would be difficult and both reactivity (TOF) and regioselectivity would be very low. In order to increase the reaction rate of hexene-1 hydroformylation, as mentioned in Section 1, one method is adding surfactant into the biphasic system. In this biphasic catalytic system, it has been found that CTAB is the best surfactant to promote the hydroformylation of α-olefin [29] selectively. When surfactant CTAB was introduced in the reaction system, CTAB would dissociate as follows:

C$_{16}$H$_{33}$N$^+$(CH$_3$)$_3$Br$^-$
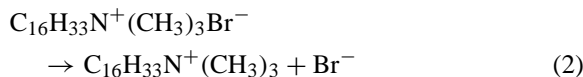
$$\rightarrow \text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3 + \text{Br}^- \quad (2)$$

Because of the amphiphilicity of C$_{16}$H$_{33}$N$^+$(CH$_3$)$_3$, most of C$_{16}$H$_{33}$N$^+$(CH$_3$)$_3$ would form micelles and exist in the interface phase between water and organic phases [29] which is beneficial to the regioselectivity. Therefore the regioselectivity obviously increases when CTAB is added. In those micelles, surfactant cation could draw catalyst anion RhCl(CO)[P(C$_6$H$_4$-m-SO$_3$$^-$)$_3$]$_2$ due to their intensive electrostatic interactions. As a result, catalyst anions are enriched in the interface, and

Rh$_{interface}$/Rh$_{total}$ would increase with the increase in the amount of added CTAB. Furthermore, increase in Rh$_{interface}$/Rh$_{total}$ would promote the coordination of substrate to rhodium and catalytic activity would increase correspondingly. The above phenomena could be summarized in Fig. 2.

However, upon addition to this reaction system, Na$_2$SO$_4$ would dissociate into Na$^+$ and SO$_4$$^{2-}$ in the aqueous phase. It would cause the equilibrium in Eq. (1) to transfer to RhCl(CO)(TPPTS)$_2$ and led the decrease of attractability between C$_{16}$H$_{33}$N$^+$(CH$_3$)$_3$ and rhodium catalyst. Therefore both Rh$_{interface}$ and catalytic activity decrease with increasing concentration of Na$_2$SO$_4$.

Derived from the intrinsic difference in affinities of different metal cations to the sulfonic anion group (–SO$_3$$^-$) in TPPTS, every metal cation causes Rh$_{interface}$/Rh$_{total}$ to decrease to a very different degree. The results in Table 3 agree with the postulate that trivalent metal cation (M^{3+}) has stronger affinity [24] to –SO$_3$$^-$ group than bivalent (M^{2+}) one, and bivalent cation than monovalent one (M$^+$).

In summary, in this biphasic hydroformylation catalyzed by RhCl(CO)(TPPTS)$_2$–TPPTS–CTAB, the addition of inorganic salts do not have obvious effects on the regioselectivity. This result is different from that obtained by Rh(I)/P[C$_6$H$_4$(CH$_2$)$_m$C$_6$H$_4$(p-SO$_3$Na)]$_3$ (m = 3, 6), which might partly be due to P[C$_6$H$_4$(CH$_2$)$_m$C$_6$H$_4$(p-SO$_3$Na)]$_3$ having the characters of TPPTS (water-solubility) and CTAB (amphiphilicity) both. Further studies on these differences are in progress.

5. Conclusions

Effect of additional inorganic salt on TOF in this biphasic system catalyzed by $RhCl(CO)(TPPTS)_2$–TPPTS–CTAB is due to the change of catalyst concentration in interface. $Rh_{interface}$, as well as TOF, is greatly influenced by different additional inorganic salts and their concentration. However, the regioselectivity does not change obviously with the kind of inorganic salts and their concentration.

Acknowledgements

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