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Synergistic effect of TPPTS and TPPDS on the regioselectivity of olefin hydroformylation in two-phase catalytic system

Hua Chen, Yaozhong Li, Junru Chen, Puming Cheng, Xianjun Li*

Department of Chemistry, Sichuan University, Chengdu, Sichuan 610064, PR China

Abstract

The hydroformylation of long-chain olefins catalyzed by the water soluble rhodium complex, $RhCl(CO)(TPPTS)_2$, were studied in aqueous/organic biphasic system containing cationic surfactants. The addition of TPPDS as a modifier dramatically increased the regioselectivity of olefin hydroformylation. A synergistic effect of TPPTS and TPPDS on the regioselectivity was observed. The ratio of linear/branched aldehyde rose from 6.5 (without TPPDS) to 22.3 ([TPPTS]/[TPPDS] = 2:1). The steric structure of hydrophilic group in the cationic surfactants exhibited an important influence on the regioselectivity. The hydrophilic group with a small steric volume was favorable for the formation of linear aldehyde. It was found that when the alkyl chain length of the higher olefin and that of the cationic surfactant were comparable (matching size), the regioselectivity for linear aldehyde was outstandingly high.

Keywords: Hydroformylation; Regioselectivity; Synergistic effect; Water soluble rhodium phosphine complex; Cationic surfactant

1. Introduction

The design and synthesis of new water soluble rhodium phosphine complex systems for two-phase catalysis have attracted a great deal of attention due to the success of the Ruhr-Chemie/Rhône-Poulenc process for hydroformylation of propene with trisulfonated triphenylphosphine, TPPTS [$P(m\text{-}C_6H_4SO_3Na)_3$], as a ligand [1–11]. The use of a water soluble catalyst is an effective means of catalyst immobilization and leads to an easy separation of catalyst from product by simple decantation after the reaction.

However, the application of water soluble catalyst is limited by the solubility of organic substrate in the aqueous phase. Thus, the rate of long-chain olefin hydroformylation drops dramatically because of its very low solubility in water. A lot of efforts have been done in order to accelerate the reaction, e.g. by introducing alcohol solvent [12,13], triphenylphosphine [14,15], modified ß-cyclodextrin [16–18] and surfactant [13–20] into two-phase catalytic system with Rh–TPPTS complexes. Among the various approaches described in the literature, the addition of cationic surfactant is the most effective for accelerating the long-chain olefin hydroformylation in a two-phase system. However, the low ratio of linear/branched aldehyde in the products does not satisfy the need for preparation of linear alcohol that are the desired products. Many rhodium complexes that contain novel water soluble phosphines and diphosphines with surface active group or/and different bite angle [21–25], thermoregulated phase-transfer ligand [26] as well as water soluble polymer ligand [27,28] have been studied. Although some rhodium complexes with water soluble diphosphine ligands exhibit excellent regioselectivity for the formation of linear aldehyde [21,24], their high prices and low

* Corresponding author. Tel./fax: +86-28-541-2904.
E-mail address: scuulixj@mail.sc.cninfo.net (X. Li).

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catalytic activities in the aqueous solution limit their application.

In this paper, we report a water soluble composite rhodium catalyst system that contains cationic surfactant as an accelerator and disodium salt of di(*m*-sulfonylphenyl)phenylphosphine, TPPDS [$C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$] as a modifier of micelle interface. The catalyst system showed high activity and very high regioselectivity for long-chain olefin hydroformylation in a two-phase system without alcohol, and at the end of the reaction, the catalyst can be separated by simple decantation.

2. Experimental

2.1. Materials

The trisodium salt of tri(*m*-sulfonylphenyl)phosphine, TPPTS [$P(m\text{-}C_6H_4SO_3Na)_3$] and the disodium salt of di(*m*-sulfonylphenyl)phenylphosphine, TPPDS [$C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$] were prepared by the method described in the literature [29]. The oxide of TPPTS and TPPDS was less than 5%. The catalyst precursor, $RhCl(CO)(TPPTS)_2$, was prepared according to the method reported by us [30]. All surfactants and organic solvents were analytical reagents. 1-Hexene and 1-docene (Sigma), as well as 1-octene and 1-dodecene (Fluka) were commercial and not treated further. Water was doubly distilled. Hydrogen (99.99%) and carbon monoxide (99%) were purchased and mixed with the ratio of 1:1 and treated with a deoxidizer and a desulfurizer prior to use.

2.2. Catalytic reaction

The typical olefin hydroformylation was conducted as follows: rhodium complex [$RhCl(CO)(TPPTS)_2$], TPPTS, TPPDS, surfactant, water and α-olefin were added into a stainless steel autoclave of 100 ml with a magnetic stirrer. The autoclave was evacuated and purged with syngas for three times. The autoclave was heated at the desired temperature and then charged with syngas at a constant pressure during the entire run. When the reaction was carried out without the compensation of syngas, the pressure would decrease during the run. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water until ambient temperature was reached. The products in organic phase were analyzed by a GC HP1890II equipped with a FID and a capillary column (30 m × 0.25 mm) SE-30.

3. Results and discussion

3.1. Synergistic effect of TPPTS and TPPDS

In order to improve the regioselectivity of long-chain olefin hydroformylation a composite catalyst system, which was composed of $RhCl(CO)(TPPTS)_2$–TPPTS–CTAB (CTAB, cetyltrimethylammonium bromide) and TPPDS was developed. If the molar ratio of total phosphine/rhodium catalyst concentration was kept constant (30:1) and the molar ratio of [TPPTS]/[TPPDS] was varied, the regioselectivity of 1-dodecene hydroformylation changed dramatically as shown in Table 1. When the phosphine ligand TPPTS or TPPDS was used alone, the ratio of linear/branched aldehyde was low. The conversion of 1-dodecene was lower than 0.5% under the same conditions in the absence of surfactants. However, when TPPTS and TPPDS were simultaneously used, a synergistic effect promoting the formation of linear aldehyde in 1-dodecene hydroformylation was observed. The highest regioselectivity could reach 95.7% at [TPPTS]/[TPPDS] = 2:1 (molar ratio). The change of [TPPTS]/[TPPDS] ratio did not obviously influence the catalytic activity. The results suggested that the addition of TPPDS caused a variation of Stern and Gauy–Chapman layer of micelle in the biphasic catalytic system. The variation of microcircumstance of micellar interface and might modify the properties of the catalyst, which could create a favorable condition for the formation of a less-crowded linear alkyl rhodium intermediate as a precursor of linear aldehyde.

3.2. Effect of CTAB concentration

The surface tension measurements of CTAB in water and in mimic reaction mixture showed that in the presence of rhodium catalyst and phosphine ligand the critical micelle concentration (CMC) of CTAB decreased from 9.6×10^{-4} mol/l at 60 °C, as reported in literature [31]. When CTAB concentration

Table 1
Effect of molar ratio of TPPTS to TPPDS on 1-dodecene hydroformylation[a]

Entry	TPPTS/TPPDS molar ratio	Aldehydes (%)	L/B[b]	L/(L + B) (%)	TOF (h^{-1})
1	TPPTS	83.4	6.5	86.7	375
2	6:1	76.7	11.1	91.7	345
3	5:1	73.6	12.1	92.4	331
4	4:1	77.5	15.5	93.9	349
5	3:1	78.5	20.3	95.3	353
6	2:1	80.1	22.3	95.7	360
7	1:1	81.7	19.9	95.2	368
8	1:2	73.6	21.5	95.5	331
9	1:3	71.2	18.3	94.8	320
10	1:4	71.2	17.6	94.6	320
11	TPPDS	84.0	5.8	85.3	378

[a] Reaction conditions: [Rh] = 1.0×10^{-3} mol/l, [CTAB] = 5.53×10^{-3} mol/l, 1-dodecene = 13.5 mmol, H_2O = 15 ml at 100 °C and 1.5 MPa (constant).
[b] Linear/branched aldehyde ratio.

was higher than its CMC, the increase of CTAB concentration would bring about the increase of micelle numbers and the expansion of the interfacial area between aqueous and organic phase. The rhodium catalyst was concentrated in the interfacial layer [13] due to the interfacial electrostatic attraction of micelle with anionic rhodium active species. The fact that the rate increased obviously with the increase of CTAB concentration as shown in Fig. 1, indicates clearly the effect of micelle number change. When CTAB concentration was higher than 2×10^{-3} mol/l, a further increase in CTAB concentration influenced the rate very little. The change of the regioselectivity also exhibited the similar tendency to that of the rate.

3.3. Effect of pressure

The effect of total pressure on the hydroformylation of 1-dodecene is summarized in Table 2. The pressure in Table 2 was the initial pressure, it decreased owing to the consumption of H_2 and CO during the reaction. Thus the data in Table 2 are different from that in Table 1 obtained at the constant pressure. The drop of pressure caused the decrease of syngas concentration

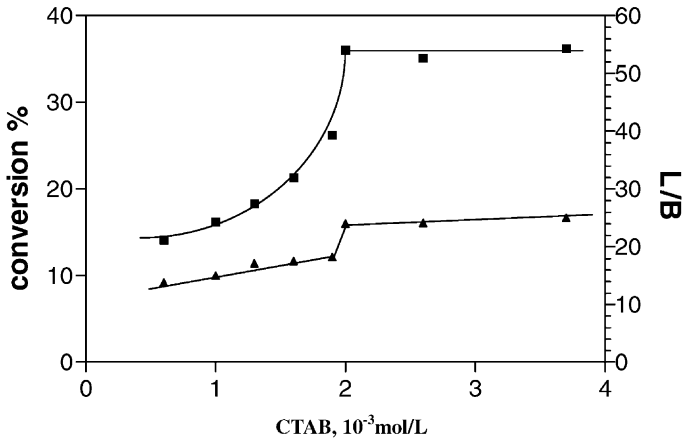

Fig. 1. Influence of CTAB concentration on the conversion and the ratio of linear/branched aldehydes (L/B) in 1-dodecene hydroformylation. [Rh] = 6.7×10^{-4} mol/l, [TPPTS]/[TPPDS] = 2:1, 1-dodecene = 13.5 mmol/l at 0.6 MPa (constant). (■) Conversion and (▲) L/B.

Table 2
Effect of the initial pressure on 1-dodecene hydroformylation[a]

	Pressure (MPa)				
	1.2	1.5	1.8	2.1	2.4
Conversion (%)	61.5	66.6	75.5	79.0	85.3
L/B	36.6	30.0	20.4	21.5	16.0
L/(L + B) (%)	97.3	96.8	95.3	95.6	94.1
TOF (h^{-1})	277	300	340	356	384

[a] Reaction conditions are the same as in Table 1 except [TPPTS]/[TPPDS] = 1:2.

and of the relative ratio of syngas/phosphine concentration in the solution. The variation was advantageous for the competitive coordination of phosphine rather than CO on rhodium atom and favorable for the formation of active rhodium species with more phosphine ligand. This reduced the rate of 1-dodecene hydroformylation, but it created a more suitable reaction microcircumstance forming linear aldehyde. Therefore, in order to reach a high regioselectivity in olefin hydroformylation a low total pressure, e.g. $\leq$1.5 MPa, should be chosen.

3.4. Effect of cationic surfactant structure

The change of cationic surfactant structure influences the catalytic activity and regioselectivity of 1-dodecene hydroformylation. The results are listed in Table 3. When the hydrophilic end of cationic surfactant was small, e.g. trimethylammonium bromide, as in CTAB, TTAB and DTAB, the regioselectivities of 1-dodecene hydroformylation were very high and the molar ratios of linear/branched aldehyde were 26–32. This could be attributed to a tight arrangement of hydrophilic groups in micellar interfacial layer. In contrast, the large steric volume of hydrophilic end of the surfactants could form a loose arrangement in the micellar interfacial layer, and the distance between the hydrophobic chains could become wider. This is favorable for the formation of branched alkyl rhodium intermediates. Thus, when TBAC was used as surfactant the molar ratio of linear/branched aldehyde decreased significantly from 32 to 8.4 because the steric volume of TBAC hydrophilic end became larger than that of TTAB. The results indicate that the interfacial structure of micelle plays a very important role in the control of regioselectivity.

Table 3
Effect of surfactant with different chain length and hydrophilic group on 1-dodecene hydroformylation[a]

	Surfactant				
	CpyB[b]	CTAB[c]	TTAB[d]	DTAB[e]	TBAC[f]
Conversion (%)	61.6	53.2	59.7	64.1	65.4
L/B	29.8	26.1	32.4	30.2	8.4
L/(L + B) (%)	96.7	96.3	97.0	96.8	89.3
TOF (h^{-1})	277	283	268	288	294

[a] Reaction conditions: [Rh] = 1.0×10^{-3} mol/l, [CTAB] = 5.53×10^{-3} mol/l, [TPPTS]/[TPPDS] = 1:2, 1-dodecene = 13.5 mmol at 1.1 MPa (constant) and 100 °C.
[b] Cetylpyridinium bromide.
[c] Cetyltrimethylammonium bromide.
[d] Tetradecyltrimethylammonium bromide.
[e] Dodecyltrimethylammonium bromide.
[f] Tetradecyl-benzyl-dimethylammonium chloride.

3.5. Matching relation between the chain length of olefin and surfactant

The data listed in Table 4 show that the olefin reactivity decreases with the increase of their chain length, however, the selectivities forming linear aldehyde increases. The results suggested that there was a relationship between the length of olefin chain and hydrophobic chain of surfactant. When their chain lengths matched, the regioselectivity of olefin hydroformylation was very high. If the hydrophobic chain in surfactant molecule was too long in comparison with olefin chain, the olefin molecule was not easily located at a suitable situation in micelle. This was not favorable for the formation of linear alkyl rhodium intermediate, and thus the regioselectivity of olefin hydroformylation decreased.

Table 4
The activity and regioselectivity of α-olefin with different chain length[a]

	Olefin			
	1-Hexene	1-Octene	1-Decene	1-Dodecene
Conversion (%)	78.6	67.2	62.0	53.2
L/B	11.5	12.6	20.9	26.1
L/(L + B) (%)	92.0	92.6	95.4	96.3
TOF (h^{-1})	354	302	324	283

[a] Reaction conditions are the same as in Table 3 except every olefin concentration is 13.5 mmol.

4. Conclusion

The investigation demonstrated that the addition of TPPDS into the biphasic catalytic system containing $RhCl(CO)(TPPTS)_2$–TPPTS–CTAB dramatically increases the regioselectivity of olefin hydroformylation. This is attributed to the synergistic effect of TPPTS and TPPDS on the microcircumstance of micelle interface. The steric volume of hydrophilic group in cationic surfactant plays also an important role in the control of regioselectivity of olefin hydroformylation. A match relationship between the length of olefin chain and hydrophobic chain of surfactant is found. Further work is in progress.

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