

Micellar effect in high olefin hydroformylation catalyzed by water-soluble rhodium complex

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Abstract

1-Dodecene hydroformylation catalyzed by water-soluble rhodium complex, $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ [TPPTS: $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$], in the presence of surfactants and alcoholic solvents was studied. The results indicated that the hydroformylation in biphasic catalytic system occurred in the interface of aqueous/organic phases. The formation of micelle was not only favorable for the reaction acceleration, but also favorable for the increase of linear aldehyde ratio in products. The key factor of the enhancement of reaction rate was the richness of rhodium catalyst in the interlayer with the static electricity attraction between active rhodium anion species and cationic end of surfactant. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydroformylation; Water-soluble rhodium complex; Biphasic catalytic system; Micelle; Surfactant; Critical micelle concentration

1. Introduction

The idea of biphasic (aqueous/organic) catalysis, which simplifies the separation of catalysts from products by decantation and facilitates catalyst recycling, has attracted great attention in recent years [1–10]. The replacement of organic solvents by water is also advantageous for environmental, safety and economical reasons. Nevertheless, there are few examples of biphasic systems with acceptable catalytic activities, and the current applications of water-soluble catalysts are limited to substrates that have

significant water solubility. The reaction rate could be reduced to such an extent that it becomes unacceptable when the solubility of the substrates in the aqueous phase is low, e.g., in the high olefin hydroformylation. Biphasic catalysis relies on the transfer of organic substrates into the aqueous phase containing the catalyst or at the interphase. Therefore, the studies have focused on improving the affinities between the two phases. The addition of co-solvents [11], such as ethanol, surfactants [12], co-ligands such as Ph_3P [10], and modified cyclodextrins [13,14], to enhance mutual solubility or mobility of the components across the phase boundary can increase the reaction rate efficiently. Recently, ligands with sur-

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factant structures, such as $\text{P}[(\text{CH}_2)_n\text{C}_6\text{H}_4\text{SO}_3\text{Na}]_3$, $\text{P}[\text{C}_6\text{H}_4(\text{CH}_2)_n\text{C}_6\text{H}_4\text{SO}_3\text{Na}]_3$, (menthyl) $\text{P}[(\text{CH}_2)_8\text{C}_6\text{H}_4\text{-}i\text{-SO}_3\text{Na}]_3$, $\text{Ph}_2\text{P}[(\text{CH}_2)_n\text{SO}_3\text{Na}]_3$, the sulfophenylalkyl derivatives of BISBI and BINAP, have been used in catalytic hydroformylation [15–19]. These ligands that have the ability to aggregate under reaction conditions and could improve the solubility of the substrates in the aqueous phase containing catalyst are superior to $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_3$ (TPPTS) for the catalytic hydroformylation of higher olefins. However, in the presence of surfactants, such as cetyltrimethylammonium bromide (CTAB), TPPTS showed higher activity [20] and much lower price for the hydroformylation of higher olefins than these ligands with surfactant structures. Moreover, the role of surfactant and the mechanism of interface reaction in biphasic system are not well-understood. For this reason, we studied the effect of the type and the concentration of surfactants on 1-dodecene hydroformylation catalyzed by water-soluble rhodium complexes with TPPTS as ligand and measured the critical micelle concentration (CMC) of CTAB in the conditions closed to which the catalytic reaction occurred.

2. Experimental

2.1. Materials

The trisodium salt of tri(*m*-sulfonphenyl)phosphine (TPPTS) was prepared in accordance with the method described in the literature [21]. The sodium salt of tri(*m*-sulfonphenyl)phosphine oxide as an impurity was less than 5%. Water content was less than 10%. The catalyst precursor, $\text{RhCl}(\text{CO})(\text{TPPTS})_2$, was prepared according to the literature [22]. All surfactants (AR) and organic solvents (AR) and 1-dodecene (Fluka) were commercial and not treated prior to use. Water was doubly distilled. Hydrogen (99.99%) and carbon monoxide (99%) were purchased and mixed directly with the ratio of

1:1 and treated with deoxidizer and desulfurizer prior to use.

2.2. Catalytic reaction

A typical procedure was conducted as follows: rhodium catalyst, TPPTS, surfactant or alcohol (if it was used), water, 1-dodecene and heptane were added to a stainless steel autoclave of 100 ml with a magnetic stirrer. The autoclave was evacuated and purged with synthesis gas for three times. The autoclave was heated at the desired temperature and then admitted synthesis gas at a constant pressure during the entire run. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water until ambient temperature. The autoclave was vented slowly, and the organic and aqueous phases were transferred to a separatory funnel. The products were analyzed by gas chromatography HP 1890II equipped with flame ionization detector (FID) and a capillary column (30 m \times 0.25 mm) SE-30.

The surface tension was measured by the maximum bubble pressure method.

3. Results and discussion

3.1. Effect of different surfactants

The results of 1-dodecene hydroformylation in the presence of different surfactants were summarized in Table 1. For comparison, the results with alcoholic solvents and without any additive were also listed. In the reaction conditions, the hydroformylation did not occur in the absence of surfactants or alcoholic solvents. Addition of cationic surfactants and alcoholic solvents enhanced dramatically the reaction rate. In contrast with the results reported in the literature [12], the addition of nonionic surfactants did not obviously enhance the rate of 1-dodecene hydroformylation and the anionic surfac-

sults suggested further that the key factor accelerating 1-dodecene hydroformylation in the presence of cationic surfactant was the richness of rhodium catalyst concentration in the interfacial layer; of course, the formation of micelle was a necessary condition.

The ratio of linear to branched aldehyde also indicated that the microcircumstances, in which catalytic reaction occurred, were different in the presence of alcoholic solvents and cationic surfactants. Evidently, in the former case, the microcircumstance was similar to the homogeneous situation, and the reactions occurred mainly in aqueous phase. However, in the presence of cationic surfactants, the catalytic reactions occurred on the interface of aqueous/organic phases. The micelle structure created an orderly and compact microcircumstance where olefin was solubilized and coordinated with rhodium complexes—which was favorable for the formation of a less-crowded linear aldehyde. If the situation were true, the change of stirring rate would cause the variation of reaction microcircumstance, which could influence the rate and selectivity of olefin hydroformylation because vigorous stirring will disturb the meta-stable micelle structure. The hypothesis was confirmed by the results listed in Table 2. The data showed that the rate constant k increased with increasing stirring rate, but the selectivity for linear aldehyde decreased, both in the case of $[TPPTS]/[Rh] = 30$ and 15, respectively. The higher stirring rate was favorable for the transfer of substrate to the interface, which increased the hydroformylation rate, but it was disadvantageous for the formation of micelle, which

Table 2
Influence of stirring rate on catalytic activity and selectivity

[TPPTS]/[Rh]	30			15		
Stirring rate (rpm)	300	400	600	400	600	
$k \times 10^3$ (/min)	6.33	8.26	8.66	9.40	9.69	
n/i	7.6	5.4	4.1	4.6	3.4	

Reaction conditions: $[Rh] = 9.6 \times 10^{-4}$ mol/l; water: 50 ml; 1-dodecene: 56.5 mmol; heptane: 12.5 ml; 1.0 MPa, 90°C; CTAB: 5.5×10^{-3} mol/l.

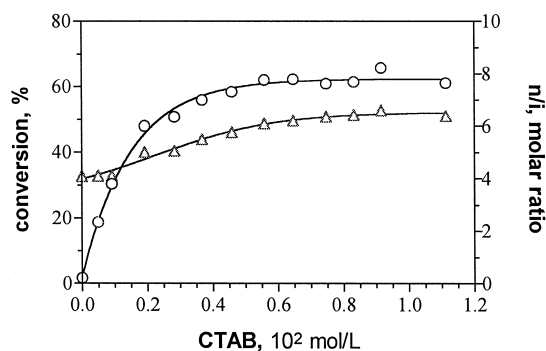


Fig. 1. Influence of CTAB concentration on 1-dodecene hydroformylation. $[Rh] = 3.53 \times 10^{-4}$ mol/l; $[P]/[Rh] = 30$, 0.5 MPa (constant); $P_{H_2}:P_{CO} = 1.2$; toluene: 5 ml; 1-dodecene: 22.6 mmol; H_2O : 30 ml; 90°C, 60 min. (○) Conversion of olefin to aldehyde. (Δ) n/i .

lowered the ratio of linear to branched aldehyde.

3.2. Influence of surfactant concentration

The influence of cationic surfactant CTAB concentration on the activity and selectivity of 1-dodecene hydroformylation in biphasic catalytic system was studied. According to the results of solvent effect [23], 1-dodecene hydroformylation in toluene as organic solvent showed the comparable activity and selectivity with in heptane. However, the presence of heptane easily caused severe emulsification of two-phase system when CTAB concentration was higher. Therefore, toluene was used instead of heptane as organic solvent in the investigation of CTAB concentration effect. The data were plotted in Fig. 1. In the beginning, the rate increased rapidly with increasing CTAB concentration. When CTAB concentration was over 2×10^{-3} mol/l, the rate increase became slow and then did not obviously change when CTAB concentration was over 4.5×10^{-3} mol/l.

To understand the variation rule, the surface tensions of CTAB solutions in water and in mimic reaction mixture were measured at 90°C and plotted in Fig. 2. From the profiles, we found CMC of CTAB to be about 1.0×10^{-3} mol/l and 0.6×10^{-3} in water and in mimic reaction mixture, respectively. The CMC of

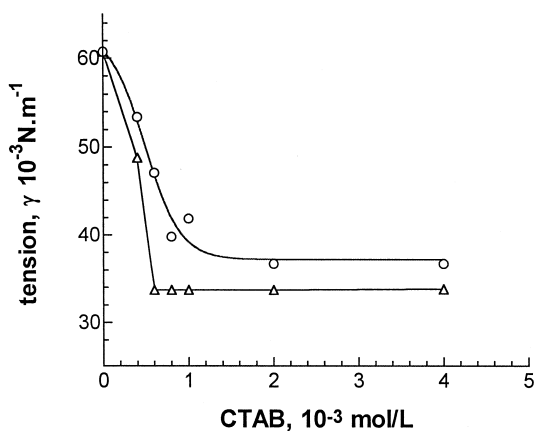


Fig. 2. Profiles of surface tension to CTAB concentration, 90°C. (○) No additive. (Δ) [Rh] = 9.6×10^{-4} mol/l; [TPPTS]/[Rh] = 16; 1-dodecene: 2.5 ml; tridecanal: 2.5 ml.

CTAB in water did not obviously change at 90°C as compared with that at room temperature (9.2×10^{-4} mol/l [24]), but the addition of rhodium complex, TPPTS and tridecanal caused the obvious decrease of CMC of CTAB in water. These results demonstrated further that the rapid increase of the rate in the reaction condition was correlated with micelle formation. When CTAB concentration was higher than CMC, the increase of CTAB concentration brought about the increase of micelle numbers and the interfacial area between two phases, as well as the concentration of rhodium complexes in the interfacial layer. This would favor the coordination between olefins and rhodium complexes and the acceleration of the hydroformylation. The further increase of CTAB concentration could induce micelle to expand and even to form O/W microemulsion in the presence of organic compounds, especially in the presence of polar aldehydes formed in the reaction [25]. Although this could also cause the increase of the interfacial area, the increase was limited because the interfacial area of micelle was much larger than that of microemulsion. It would induce slow increase of catalytic species concentration on the interfacial layer. Therefore, the rate increase became gradually slow and almost reached constant at high CTAB concentration.

4. Conclusion

The study demonstrated that 1-dodecene hydroformylation in biphasic catalytic system occurred in the interface of aqueous/organic phases. The formation of micelle was not only favorable for the reaction acceleration, but also favorable for the increase of linear aldehyde ratio in products. The key factor of the enhancement of reaction rate was the richness of rhodium catalyst in the interfacial layer with the static electricity attraction between active rhodium anion species and cationic end of surfactant.

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