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阳离子表面活性剂存在下水/有机两相体系中双环戊二烯氢甲酰化

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摘要: 研究了在阳离子表面活性剂存在下水/有机两相中水溶性铑配合物 $RhCl(CO)(TPPTS)_2$ (TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$) 催化双环戊二烯氢甲酰化反应, 考察了反应温度、催化剂浓度、不同水溶性膦配体 TPPTS 和 TPPDS ($C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$), 以及表面活性剂结构对催化反应的影响. 结果表明, 配体 TPPTS 比 TPPDS 表现出更好的助催化效果; 阳离子表面活性剂 $C_{16}H_{33}N(CH_3)_2C_nH_{2n+1}Br$ ($n = 1, 8, 12, 16$) 的加入可大大加速反应, 但加速作用随着其中 $C_nH_{2n+1}Br$ ($n = 1, 8, 12, 16$) 链长的增加而减弱; 在阳离子表面活性剂 (0.05~5.00 mmol/L) 存在下, 双环戊二烯的转化率随表面活性剂浓度的增加先增加后降低. 含催化剂的水相循环使用 4 次后, 催化活性和区域选择性没有明显下降.

关键词: 水/有机两相体系; 双环戊二烯; 氢甲酰化; 铑; 表面活性剂

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Dicyclopentadiene Hydroformylation in an Aqueous/Organic Two Phase System in the Presence of a Cationic Surfactant

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Abstract: Dicyclopentadiene (DCPD) hydroformylation catalyzed by the water soluble rhodium complex $RhCl(CO)(TPPTS)_2$ (TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$) was studied in an aqueous/organic two phase system containing a cationic surfactant. The effects of various reaction parameters such as reaction temperature, catalyst concentration, water soluble phosphine TPPTS or TPPDS ($C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$), and surfactant structure were examined. The catalytic activity was better with the ligand TPPTS than with TPPDS. The reaction was accelerated by the addition of the cationic surfactant $C_{16}H_{33}N(CH_3)_2C_nH_{2n+1}Br$ (n = 1, 8, 12, 16) but the accelerating effect was attenuated with an increase of the n value. In the presence of the surfactant, the DCPD conversion increased initially and then decreased as the rhodium concentration increased in the range of 0.05–5.00 mmol/L. The catalyst containing aqueous phase was reused four times without significant decrease in activity and regioselectivity.

Key words: aqueous/organic two phase system; dicyclopentadiene; hydroformylation; rhodium; surfactant

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Dicyclopentadiene (DCPD) hydroformylation produces mono- and diformyl derivatives, which are hydrogenated to produce the corresponding carbinols. The carbinols are used as raw materials for agricultural chemicals, lubricating oil, plasticizer, and also as intermediate materials for pharmaceuticals and perfumes. For instance, the monocarbinols are valuable precursors for the synthesis of 4-homoisoteistane derivatives, which have powerful antiviral activity [1,2]. Since there are two unsaturated double bonds in its molecular structure, the products of DCPD hydroformylation are generally very complicated. Nevertheless, the greater reactivity of the more strained norbornenyl moiety probably directs the reaction mainly to the 8, 9 double bond [3]. Inamoto and coworkers [3] found that a rhodium triphenylphosphine complex can catalyze regioselective hydroformylation under relatively mild conditions, and obtained a mixture of 8- and 9-formyltricyclo [5,2,1,$0^{2,6}$]dec-3-ene (referred to as MFTD, Scheme 1) with over 80% yield.

Aqueous/organic two phase hydroformylation can facilitate the separation of the catalyst from the product. More importantly, the water solvent is environmentally friendly and meets the demand for green chemistry. Hydroformylation in the aqueous/organic two phase system has been extensively studied. The most successful industrial application is Rh-TPPTS (TPPTS: P(m-$C_6H_4SO_3Na)_3$) catalyzed propene hydroformylation, namely, the Ruhrchemie Rhône-Poulec (RCH/RP) process [4,5]. However, a relatively low activity was obtained with olefins with poor water solubility. There are several ways to improve the water solubility of these olefins, such as adding co-solvent [6], co-ligand [7], amphiphilic phosphines [8–11], modified cyclodextrin [12–14], thermo-regulated phase transfer catalyst [15,16], and surfactants [17–25], to accelerate the aqueous/organic two phase hydroformylation. However, both the co-solvent and co-ligand inevitably lead to the loss of the catalyst. The synthesis of amphiphilic phosphine is usually tedious. The usage of modified cyclodextrin often provides poor regioselectivity. Therefore, the addition of a surfactant is more promising because this is usually commercially available and the synthesis method is relatively easy. Previously, we reported [21] that a cationic surfactant can effectively accelerate Rh-TPPTS catalyzed high olefin hydroformylation, especially when the surfactant concentration is higher than its critical micelle concentration (CMC). The reason was attributed to two factors: (1) the formation of the micelle increased the interfacial area of two phases and solubility of high olefins in the aqueous phase containing the rhodium complex; (2) the micelle cationic head groups were oriented towards the aqueous phase and formed a positively charged ion layer, which attracted active rhodium complex anion species to the interfacial layer from the aqueous solution. Thus, the catalyst was highly concentrated in the interfacial layer and could easily interact with olefin solubilized in the micelles. DCPD hydroformylation usually shows relatively low activity in an aqueous/organic two-phase system due to the poor solubility of DCPD in the water phase. The addition of a cationic surfactant is a feasible way to accelerate the reaction. However, only few research works in this area have been reported [26]. There is no report about the effect of the surfactant structure on DCPD hydroformylation. In this paper, we carried out DCPD hydroformylation catalyzed by the rhodium complex $RhCl(CO)(TPPTS)_2$ in an aqueous/organic two phase system. A strategy for accelerating the reaction by adding the cationic surfactants $C_{16}H_{33}N(CH_3)_2C_nH_{2n+1}Br$ (n = 1, 8, 12, 16) is presented. Various reaction factors, such as reaction temperature, catalyst concentration, type of ligand, and the surfactant structure were investigated.

1 Experimental

1.1 Materials

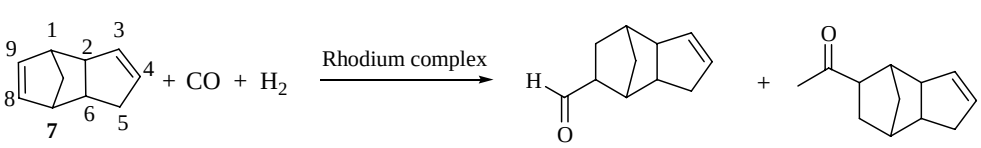
The water soluble ligands TPPTS and TPPDS ($C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$), and the complex $RhCl(CO)(TPPTS)_2$ were prepared by following published methods [28]. Other reagents were purchased from commercial sources and used as received.

1.2 Surface tension experiment

The surface tension γ was determined by the maximum bubble pressure method at 28 °C. The pressure was measured with a precision digital pressure gauge (Sang Li Electronic Equipment Factory, Nanjing, China)

1.3 Hydroformylation test

The hydroformylation reactions were performed in a 60 ml stainless steel autoclave with a magnetic stirrer. Known



Scheme 1. DCPD hydroformylation catalyzed by a rhodium phosphine complex.

Table 1 Effect of temperature on DCPD hydroformylation

Entry	Temperature (°C)	Conversion of DCPD (%)	Selectivity[a] (%)	E/L[b]	Color of the organic phase
1	60	17.7	93.0	1.2	colorless
2	80	51.1	93.2	1.2	colorless
3	100	89.2	94.6	1.1	colorless
4	120	99.1	95.2	1.2	light yellow
5	140	99.3	95.2	1.2	tea color

Reaction conditions: n(Rh) = 1.0 mmol/L, n(TPPTS)/n(Rh) = 35, n(CTAB) = 1.0 mmol/L, $V(H_2O)$ = 3.0 ml, V(DCPD) = 1.0 ml, $p(CO+H_2)$ = 1.5 MPa, 1 h.

[a]Selectivity to 8- and 9-formyltricyclo [5,2,1,$0^{2,6}$] dec-3-ene. [b]Molar ratio of earlier isomer of MFTD to the latter isomer.

amounts of $RhCl(CO)(TPPTS)_2$, TPPTS, DCPD, surfactants, and water were added into the autoclave. After the autoclave was evacuated and purged with syngas three times, it was pressurized with the required volume of syngas (CO/H_2 = 1:1) and held at the desired temperature. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water to ambient temperature.

A HP 1890 series II gas chromatograph (Hewlett Packard, Palo Alto, CA) equipped with a flame ionization detector was used for product analysis. The separation was done on a SE-30 (30 m × 0.32 mm) fused silica capillary column.

2 Results and discussion

The product characterization was performed by the GC-MS instrument. Similarly to the results reported by Inamoto and coworkers, DCPD hydroformylation produced two major products, 8- and 9-formyltricyclo [5,2,1,$0^{2,6}$] dec-3-ene. Although the isomers of MFTD were separated on the gas chromatographic column, their individual identities could not be determined. We used the letter 'E' to denote the earlier isomer and 'L' to denote the later isomer according to the retention time of the isomers.

2.1 Effect of temperature

The preliminary experiment was carried out at 1.5 MPa initial syngas in the presence of 1.0 mmol/L cetyltrimethylammonium bromide (CTAB). The temperature range from 60 to 140 °C was investigated in order to test the effect of the temperature on DCPD hydroformylation. At temperatures lower than 80 °C, the DCPD conversion was very low after 1 h reaction time (Table1, Entries 1 and 2). This increased with temperature increasing. The DCPD was almost completely converted at 120 °C. However, at this temperature the organic phase exhibited a light yellow color (Table 1, Entry 4), which indicated a loss of the rhodium complex into the organic phase. Therefore, the reaction temperature was set at 100 °C in the following experiments.

Table 2 Effect of the rhodium concentration on DCPD hydroformylation

Entry	Concentration of Rh (mmol/L)	Conversion of DCPD (%)	Selectivity (%)	E/L
1	0.05	6.4	95.2	1.1
2	0.10	20.5	92.6	1.2
3	0.50	97.5	95.3	1.2
4	1.00	89.2	94.6	1.1
5	5.00	73.3	94.2	1.1

Reaction conditions are the same as in Table 1.

2.2 Effect of the rhodium complex concentration

The effect of rhodium complex concentration on DCPD hydroformylation was tested in the range of 0.05–5.00 mmol/L. The results are shown in Table 2. With the rhodium complex concentration at 0.05 mmol/L, only 6.4% of DCPD was converted in 1 h (Table 2, entry 1). This suggested that a sufficient rhodium complex concentration was required to ensure an acceptable activity. The conversion was increased significantly to 97.5% when the concentration of the rhodium complex was increased to 0.50 mmol/L. This can be attributed to more reaction active sites available with increased rhodium complex concentration. However, the further increase of the concentration led to a decrease in the activity. The reason was probably due to the large amount of TPPTS added to the system to maintain the molar ratio of TPPTS/Rh at a fixed value (in this case, TPPTS/Rh = 35). The TPPTS concentration was as high as 175 mmol/L when the rhodium complex concentration was increased to 5 mmol/L. Due to its high ionic charge, TPPTS dissolved in the aqueous phase was detrimental to the stability of the CTAB micelle. The CMCs of CTAB in the different systems were evaluated by a surface tension technique. The experiments were carried out at 28 °C, and the CMCs of CTAB were 1.1, 0.9, and 2.7 mmol/L, respectively, in the three different systems (Fig. 1). For the system with the $RhCl(CO)(TPPTS)_2$ concentration of 5.0 mmol/L and TPPTS/Rh molar ratio at 35, the increased CMC may be responsible for the lower reaction rate. The CTAB concentration in this catalysis system was only 1.0 mmol/L, which

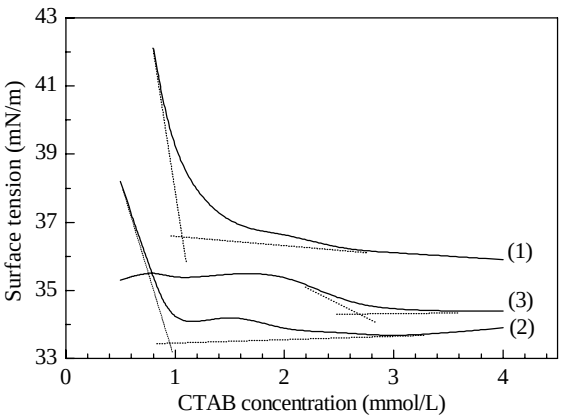


Fig. 1. Surface tension profiles of aqueous solutions of CTAB containing different amounts of $RhCl(CO)(TPPTS)_2$ and TPPTS. (1) CTAB aqueous solution; (2) CTAB aqueous solution containing 0.5 mmol/L of $RhCl(CO)(TPPTS)_2$ and 17.5 mmol/L of TPPTS; (3) CTAB aqueous solution containing 5.0 mmol/L of $RhCl(CO)(TPPTS)_2$ and 175.0 mmol/L of TPPTS.

was far lower than the CMC (2.7 mmol/L) and therefore it could not accelerate the reaction effectively.

2.3 Effect of the phosphine ligand

Apart from reaction parameters such as temperature and catalyst concentration, the ligand present can also influence the reaction. We previously reported [20] that the addition of TPPDS into the $RhCl(CO)(TPPTS)_2$-TPPTS catalyzed 1-dodecene hydroformylation system containing the surfactant CTAB can effectively increase the linear to branched molar ratio of the product aldehyde. To investigate the effect of TPPDS on DCPD hydroformylation, the molar ratio of TPPDS/TPPTS was varied with the total phosphine to rhodium ratio at a constant value (35:1). The data is collected in Table 3. In the case of the phosphine TPPTS or TPPDS used alone, the ratio of E/L aldehyde was as low as 1.1. When TPPTS and TPPDS were simultaneously used, a promoting effect on the E/L aldehyde was observed, although it only increased slightly (Table 3, entries 2–8). However, it is worth noting that the DCPD conversion changed remarkably, as shown in Table 3. The conversion of DCPD decreased gradually with decreasing molar ratio of TPPTS/TPPDS. With TPPTS as the ligand, 89.2% of DCPD was hydroformylated in 1 h reaction time. In contrast, only 44.5% of DCPD was converted into the corresponding aldehyde when TPPDS was used instead. There are fewer electronic withdrawing groups ($-SO_3Na$) in the TPPDS ligand than in the TPPTS ligand, and TPPDS is more basic. The effect of the TPPDS ligand on the DCPD conversion was in good agreement with the general observation that a more basic phosphorous ligand resulted in lower activity [29]. The lower conversion in the case of TPPDS as the ligand perhaps can also be attributed to the hydrophobic phenyl group in TPPDS. The phenyl group can penetrate into the posterior layer of the micelle, and the DCPD solubilized in the micelle need to overcome the steric hindrance resulting from the phenyl group of TPPDS before it can reach the interface to coordinate with the rhodium active center (Fig. 2). Therefore, the reaction was slowed down.

Table 3 Effect of molar ratio of TPPTS to TPPDS on DCPD hydroformylation

Entry	*n*(TPPTS)/*n*(TPPDS)	Conversion (%)	Selectivity (%)	E/L
1	TPPTS	89.2	94.6	1.1
2	10:1	88.0	95.0	1.4
3	7.5:1	86.1	93.7	1.4
4	5:1	85.8	94.5	1.3
5	1:1	86.7	94.6	1.2
6	1:5	75.7	94.2	1.3
7	1:7.5	70.7	94.1	1.3
8	1:10	63.8	94.0	1.3
9	TPPDS	44.5	93.1	1.1

Reaction conditions are the same as in Table 1 except *n*(TPPTS+TPPDS)/*n*(Rh) = 35.

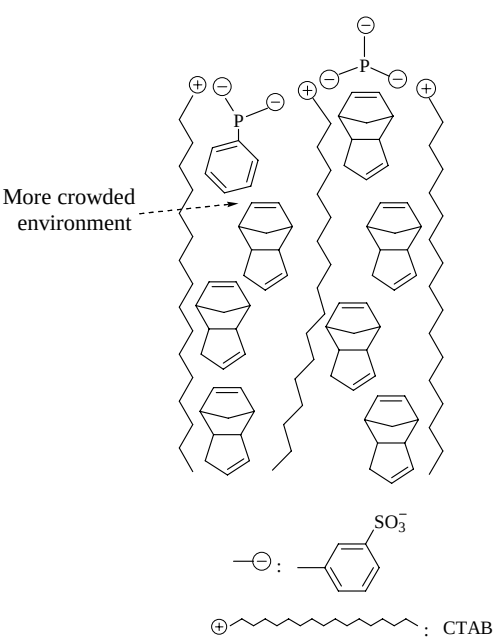


Fig. 2. Sketch of the possible position of TPPDS and TPPTS in CTAB micelles and the effect on DCPD hydroformylation.

2.4 Effect of the surfactant structure

The effect of the surfactant on the reaction was also examined. Without CTAB, only 41.0% of DCPD was converted after reaction for 1 h under 2.0 MPa syngas pressure, which was much lower than the conversion in the presence of CTAB (98.2%, Table 4, entry 2). For comparing with CTAB, a series of cationic surfactant $C_{16}H_{33}N(CH_3)_2$-

Table 4 Effect of surfactant on DCPD hydroformylation

Entry	Surfactant	Conversion (%)	Selectivity (%)	E/L
1	—	41.0	94.6	1.2
2	$C_{16}H_{33}N(CH_3)_2CH_3Br$	98.2	93.0	1.1
3	$C_{16}H_{33}N(CH_3)_2C_8H_{17}Br$	89.4	94.3	1.1
4	$C_{16}H_{33}N(CH_3)_2C_{12}H_{25}Br$	81.9	94.6	1.0
5	$C_{16}H_{33}N(CH_3)_2C_{16}H_{33}Br$	74.1	93.9	1.1

Reaction conditions are the same as in Table 1 except $p(CO+H_2)$ = 2.0 MPa.

$C_nH_{2n+1}Br$ (n = 8, 12, 16) were tested. The results are shown in Table 4. The DCPD conversion decreased as the n value in $–C_nH_{2n+1}$ increased from 1 to 16. This was completely different from the observation in the long chain olefin hydroformylation system. In the latter case, the long chain olefin conversion increased with the lengthening of the alkyl chain $–C_nH_{2n+1}$ [16]. This was explained by that the double long chained surfactant $C_{16}H_{33}N(CH_3)_2C_nH_{2n+1}Br$ (n = 12, 16) can form a vesicle, which not only can dissolve more olefin, but also can enlarge the interface to a larger extent than the micelle formed by CTAB. Consequently, the double long chained surfactant can accelerate the reaction much significantly. As compared with a flexible long chain olefin, it is more difficult for the more sterically demanding DCPD to move to the interface from the hydrophobic region. Furthermore, the alkyl group $–C_nH_{2n+1}$ may block the contact of the catalyst with DCPD more with the lengthening of the alkyl chain (Fig. 3).

2.5 Catalyst recycling

The surfactant can cause problems for the recycling of the rhodium catalyst due to the mutual solubility of the organic and aqueous component. The yellowish color of the organic phase at a relatively lower molar ratio of P/Rh showed leaching of the rhodium complex into the organic phase. Our previous study [24] demonstrated that rhodium complex leaching can be alleviated at the expense of using a larger amount of water-soluble ligand. For this reason, the molar ratio of P/Rh in previous experiments was set at a relatively high value (P/Rh = 35). However, the amphiphilic CTAB will dissolve partially in the organic phase and the amount in the aqueous phase decreased after the reaction. To ensure the concentration of the CTAB was above that of the CMC, additional CTAB was added in the recycling experiment. Simultaneously, an amount of TPPTS was added in order to immobilize the catalyst. With the addition of both the CTAB and TPPTS, the recovered aqueous phase containing the catalyst was reused in four recycling experiments. There was nearly no loss of activity and selectivity (Table 5). The rhodium complex concentration in the organic phase determined by the ICP method was about 0.9×10^{-6}. Only 0.3% of the initial amount of rhodium was lost to the organic phase in the reaction.

Table 5 Catalyst recycle tests

Recycling run	CTAB/TPPTS (mg/mg)	Conversion (%)	Selectivity (%)	E/L
1	—	95.2	93.9	1.2
2	0.9/11.4	98.6	94.6	1.2
3	0.5/22.4	98.9	94.7	1.2
4	0.9/20.2	98.8	94.0	1.2
5	0.6/20.1	98.3	94.9	1.2

Reaction conditions are the same as in Table 1 except $p(CO+H_2)$ = 2.0 MPa.

3 Conclusions

The effects of the surfactant structure and type of ligand on DCPD hydroformylation in a water/organic two phase system were studied. Due to the sterically demanding structure of DCPD, a relatively looser micelle micro-environment will give better catalytic activity. Accordingly, the ligand TPPTS showed a better catalytic activity than the TPPDS ligand. For the same reason, the accelerating effect of the surfactant $C_{16}H_{33}N(CH_3)_2$-$C_nH_{2n+1}Br$ (n =1, 8, 12, 16) decreased as the n value increased. The catalyst recycling test showed that the aqueous solution containing

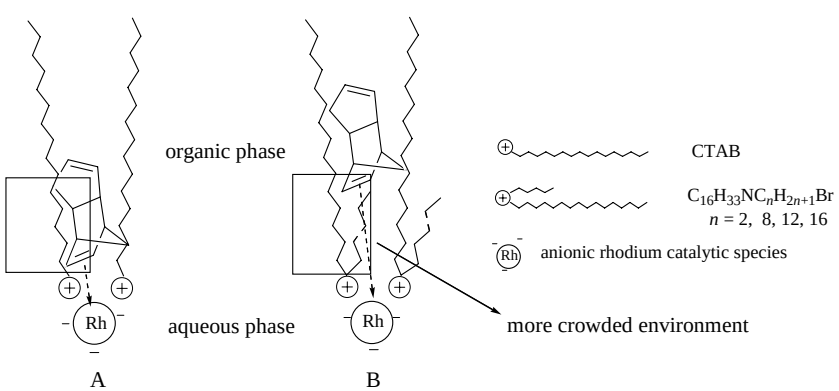


Fig. 3. Illustration of the effect of surfactant structure on DCPD hydroformylation.

the rhodium complex could be reused four times by adding appropriate amounts of surfactant and ligand.

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