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Hydroformylation of 2,5-norbornadiene in organic/aqueous two-phase system and acceleration by cationic surfactants

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The organic/aqueous biphasic hydroformylation of 2,5-norbornadiene (NBD) was investigated for the first time using HRh(CO) (TPPTS)₃ (TPPTS: trisodium salt of tri(*m*-sulphonylphenyl)phosphine) as the catalyst precursor. A comparison was made of homogeneous and biphasic systems. The optimum reaction parameters are discussed and the reaction mechanism is presented. In order to ensure the process attained high activity under moderate conditions, the effect of various cationic surfactants was tested in the biphasic hydroformylation of NBD. The results indicated that the hydroformylation of NBD in the biphasic system exhibited high activity and high selectivity to dialdehyde products under mild conditions. The addition of cationic surfactants markedly accelerated the reaction. A single long-chain surfactant seemed to exert a greater impact on the hydroformylation of NBD than a double long-chain surfactant. Moreover, the recycling of aqueous solution containing catalyst with or without surfactant was investigated. In the absence of the surfactant, the aqueous catalyst could be recycled six times without a significant decrease in activity and selectivity. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: 2,5-norbornadiene; biphasic hydroformylation; water-soluble phosphine rhodium complex; surfactants; high added value

Introduction

With a production of approximately 12 million tons per year, the hydroformylation of olefins (also named the oxo process) is generally recognized as one of the most significant catalytic reactions.^[1] The products of this reaction and their derivatives are widely used in the synthesis of plasticizers, pharmaceutical intermediates and many other fine chemicals.^[2]

Recently, much attention has been concentrated on the hydroformylation of special olefins because of its high added value in the manufacture of fine chemicals.^[3-14] Thus, the hydroformylation of 2,5-norbornadiene (NBD) is of interest, since the carboxylated derivatives of its dialdehyde products are applied in the manufacture of advanced photoelectron instruments.^[15] Additionally, NBD is a very intriguing alkene on account of its unique stereochemical structure and its ability to form stable complexes with rhodium metal.^[16] The unconiugated two internal double bonds can allow the production of mono- and diformyl derivatives (Scheme 1). Monoaldehydes are mixtures of exo- and endo-aldehydes while dialdehydes are mixtures of 2,5- and 2,6-dialdehydes. Saus et al. reported the photochemical hydroformylation of NBD catalyzed by HRhCO (PPh₃)₃-PPh₃, which suggested that 95% conversion was achieved only when the reaction pressure reached 8.0 MPa and a long reaction time of 50 h was required.^[17] Later, homogeneous hydroformylation of NBD using the same catalyst precursor gave an excellent result while the reaction pressure was as high as 10.0 MPa.^[18] In addition to the harsh requirements being totally unfavorable for industrialized manipulation, the separation process for products and catalyst would also be

troublesome, since the dialdehyde products have a high boiling point of 280°C. Hence, the separation of products from catalyst in the homogeneous catalysis method would undoubtedly cause a loss of catalyst.

Our group has long been interested in organic/aqueous biphasic hydroformylation owing to its superiority in terms of easy separation of the costly catalyst from the products after the reaction. Also, using water as solvent is environmentally friendly and green.^[19,20] Therefore, we tried to use a moderate organic/aqueous biphasic process to conduct the hydroformylation of NBD using HRh(CO)(TPPTS)₃–TPPTS (TPPTS: trisodium salt of tri(*m*-sulphonylphenyl)phosphine) as catalyst. In the work reported here, the effect of reaction conditions was fully investigated for the biphasic hydroformylation of NBD and the reaction mechanism was investigated. Since the poor water solubility of NBD made it hard for it to contact the catalyst in the aqueous phase, also the effect of cationic surfactant was studied in the biphasic hydroformylation of NBD, inspired by our previous work.^[21–24]

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Dialdehydes

Selectivity (%)^d

Monoaldehydes



Scheme 1. Hydroformylation of 2,5-norbornadiene (NBD).

Experimental

Materials and instrumentation

The catalyst precursor HRh(CO)(TPPTS)₃,^[25] the wate TPPTS^[25] and the surfactants docosyltrimethylamn (DTAI),^[26] didodecyldimethylammonium bromide cetyldodecyldimethylammonium bromide (DCDAB) dimethylammonium bromide (DCMAB)^[26] were prep to the literature and their structures were confirmed their ¹H NMR and ³¹P NMR spectra with those of NBD (Alfa), dodecyltrimethylammonium bromide cetyltrimethylammonium bromide (CTAB; Sigma) and chloride monohydrate (CPC; Alfa) were commercially used without purification. Distilled and deionized w in all experiments. Hydrogen (99.9%) and carbon mc were premixed with a pressure ratio of 1 to 1.

The hydroformylation products were analyzed using GC with an Agilent 6890 equipped with a flame ionization detector and a capillary column (CP-SIL 5cb, 25 m \times 0.53 mm). The products were identified using GC-MS. The rhodium content in the solution was determined using inductively coupled plasma (ICP) atomic emission spectrometry with an IRIS Advantage.

Hydroformylation and catalytic recycling

The hydroformylation was carried out in a 60 ml stainless steel autoclave with a magnetic stirrer. HRh(CO)(TPPTS)₃, TPPTS, surfactant, organic solvent, olefin and distilled water were added in sequence. The autoclave was purged with syn-gas (H_2 :CO = 1:1) three times. The reaction was carried out under the desired pressure and temperature with stirring for a desired time. When the reaction was completed, the autoclave was cooled to room temperature using cold water and the redundant syn-gas was vented. The reaction mixture was transferred to a tube, and the upper organic layer was carefully taken out and analyzed using GC.

After the upper organic phase had been carefully removed, the catalyst-containing agueous phase was recharged in the stainless steel autoclave with fresh olefin and organic solvent. Then, the steps as described above were carried out. The concentration of rhodium leaching into the organic phase was determined using the ICP method.

Results and discussion

In order to investigate how NBD hydroformylation behaves in organic/aqueous biphasic and homogeneous systems, preliminary experiments were conducted using water-soluble HRh(CO) (TPPTS)₃-TPPTS as biphasic system and oil-soluble HRh(CO) (TPP)₃-TPP as homogeneous system, respectively. In both cases, the hydroformylation of NBD proceeds smoothly under the same moderate reaction conditions.

As evident from Table 1, the hydroformylation products of NBD are composed of monoaldehydes and dialdehydes. A few hydrogenation products of NBD are also present. Surprisingly, the

	1 2	Rh–TPPTS ^a Rh–TPP ^b	51.7 31.0	12.8 25.6	86.0 73.3	
r-soluble ligand nonium iodide (DDMAB), ^[26] ^{26]} and dicetyl- pared according t by comparing	^a Reaction conditions: $[HRh(CO)(TPPTS)_3] = 6.1 \times 10^{-4} \text{ mol } I^{-1} \text{ in 2 ml of } H_2O, [TPPTS]/[Rh] = 50 (molar ratio), NBD = 0.5 ml (4.9 mmol), toluene 1.5 ml, 70°C, 2.0 MPa, 120 min. b Reaction conditions: [HRh(CO)(TPP)_3] = 6.1 \times 10^{-4} \text{ mol } I^{-1} \text{ in 2 ml of toluene, } [TPP]/[Rh] = 50 (molar ratio), NBD = 0.5 ml (4.9 mmol), 70°C, 2.0 MPa, 120 min. c Conversion of NBD based on GC. d Selectivity of mono- or dialdehydes.$					
I by comparing f the literature. (DTAB; Sigma), I cetylpridinium y obtained and vater was used pnoxide (99.0%)	hydro bette tion r the re	oformylation of N r than that in the ate and selectivit eaction mechanis	NBD in the bip homogeneou y to dialdehyd m of the bipha	phasic system pr is system. It has es, which led us asic NBD hydrofo	oceeds much a higher reac- to investigate ormylation.	
ing CC with an						

systems

Entry Catalyst

Mechanism of NBD hydroformylation

Since final products are a mixture of monoaldehydes and dialdehydes, the variation in the reaction time was investigated. The results show that the reaction time exerts a very great impact on the substrate conversion, and also affects the product distribution (Table 2). As the reaction time increases from 0.5 to 7.0 h, the conversion increases dramatically from 9.9 to 99.9%.

Table 1. Hydroformylation of NBD in biphasic and homogenous

Conversion (%)^c

However, it is worth noting that the selectivity of monoaldehydes and dialdehydes changes following a reverse trend with increasing conversion. The monoaldehyde selectivity decreases quickly, and, at its expense, the selectivity of dialdehydes increases to dominate the ratio. In addition, even for a reaction time as short as 0.5 h, where only 9.9% of NBD is converted to aldehydes, the selectivity of dialdehydes still reaches 40.6%. This phenomenon might indicate that dialdehydes are more easily formed from monoaldehyde and that the two double bonds of NBD are not simultaneously hydroformylated. The mechanism is supposed to be that the NBD firstly reacts with syn-gas to form monoaldehydes which are then converted into dialdehydes. The detailed mechanism is shown in Fig. 1, referring to the well-known hydroformylation kinetics and mechanism of ordinary olefins.

Table 2.	Effect of reaction time on biphasic hydroformylation of NBD					
Entry	Reaction time (h)	Conversion (%)	Selectivity (%)			
			Monoaldehydes	Dialdehydes		
1	0.5	9.9	58.3	40.6		
2	1.0	30.6	29.9	67.9		
3	2.0	51.7	12.8	86.0		
4	3.0	81.4	7.1	91.1		
5	5.0	99.1	3.9	95.2		
6	7.0	99.9	2.1	97.0		
7	10.0	99.9	2.0	97.5		

Reaction conditions are the same as in footnote of Table 1 except the reaction time.



Figure 1. Proposed mechanism of NBD hydroformylation catalyzed by HRh (CO)(TPPTS)₃.

As shown in Fig. 1, it is suggested that NBD is easily coordinated with the Rh complex to form the stable intermediate **2'** which makes it difficult to transfer to the active species **2** in the homogeneous system. In contrast, the low concentration of NBD in water and the more bulky TPPTS would inhibit the formation of intermediate **2'** in the aqueous biphasic system. In this case the formation of less stereo-hindered species **2** is more favorable, and as a consequence the NBD hydroformylation has higher activity in the aqueous biphasic system than in the homogeneous system (Table 1).

Effect of reaction parameters

The effect of reaction parameters such as temperature, syn-gas pressure and molar ratio of phosphine to Rh on the hydroformylation of NBD was investigated in detail to determine the optimal reaction conditions.

As evident from Table 3 (entries 1–3), reaction temperature markedly affects the hydroformylation of NBD in the aqueous biphasic system. The conversion of NBD increases rapidly with increasing temperature. The conversion is only 10.1% when the reaction temperature is 50°C. Products contain monoaldehydes and dialdehydes. When the temperature increases to 90°C, 95.5% of the substrate is converted to aldehydes and the selectivity of dialdehydes is up to 94.1%. However, the color of the organic phase becomes light yellow, which suggests that the aqueous catalyst could leach

Lindy	/ (C)	/ (IVII U)	1 / 1 11	(%)	Selectivity (76)	
					Monoaldehydes	Dialdehydes
1	50	2.0	50	10.1	50.5	48.5
2	70	2.0	50	51.7	12.8	86.0
3	90	2.0	50	95.5	4.8	94.1
4	70	1.0	50	29.0	30.0	65.9
2	70	2.0	50	51.7	12.8	86.0
5	70	3.0	50	50.9	13.5	85.3
6	70	4.0	50	47.7	15.3	83.2
7	70	2.0	3	6.7	58.2	35.1
8	70	2.0	10	14.5	37.2	56.4
9	70	2.0	20	69.4	7.6	89.5
10	70	2.0	35	75.5	5.7	93.4
2	70	2.0	50	51.7	12.8	86.0
11	70	2.0	60	29.1	28.4	70.0
12	70	2.0	70	25.7	27.9	69.0
Reaction conditions are the same as in footnote of Table 1 except the						

Table 3. Effect of temperature, pressure and P/Rh molar ratio on

biphasic hydroformylation of NBD Entry $T(^{\circ}C) = P(MPa) = P/Bh - Conversion$

Reaction conditions are the same as in footnote of Table 1 except the corresponding reaction parameters.

into the organic phase and the active catalytic metal species suffers a huge loss. And the ICP result confirms the leaching of Rh of 4.13 ppm (6.60%), which is unacceptable from the point of view of catalyst stability. Hence a moderate temperature of 70° C was employed in the following studies.

The effect of syn-gas pressure was investigated (Table 3, entries 4–6). The substrate conversion exhibits a large jump from 29.0 to 51.7% when the pressure increases from 1.0 to 2.0 MPa. However, further increase in pressure causes a slight decrease in the conversion of NBD. This might be attributed to the excess carbon monoxide preventing the forward coordination of NBD with the Rh active species, thus lowering the reaction rate.

As is known, the amount of auxiliary ligand usually affects the reaction rate and product distribution in biphasic hydroformylation.^[2] Therefore, the effect of the TPPTS/Rh molar ratio was also investigated. The results (Table 3, entries 7–12) suggest that the conversion of NBD increases quickly with an increase of TPPTS/Rh molar ratio. The highest conversion and selectivity of dialdehyde (75.5 and 93.4%, respectively) are achieved at a molar ratio of 35. Further increase causes distinct decreases in both the conversion and the selectivity of dialdehyde. As the molar ratio of TPPTS/Rh reaches 70, the conversion is reduced to 25.7% with the selectivity towards dialdehyde decreasing to 69.0 from 93.4% (Table 3, entry 12 versus entry 10).

This might be ascribed to the complex equilibrium of complicated rhodium species present in the biphasic medium, and the ligand concentration could be appropriately adjusted to produce the catalytic active species. At a lower ligand concentration, the Rh active species is hardly generated, thus only marginal aldehydes are detected at a P/Rh ratio of 3 (Table 3, entry 7). Increasing the P/Rh ratio possibly shifts the equilibrium towards the direction where more Rh active species is formed. The highest conversion at a TPPTS/Rh ratio of 35 is probably attributed to the overwhelming amount of the catalytic active species. Further increase in TPPTS would block the coordination sites of the central metal and inhibit

Salactivity (%)

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the coordination of the NBD substrate with rhodium, which decreases the substrate conversion.

However, also to be taken into account is the chelated coordination mode of NBD, which would even coordinate with rhodium in the aqueous phase when they are separated in two immiscible phases. This might explain the fact that the biphasic hydroformylation of NBD proceeds well even in the absence of any additive for improving the solubility of the substrate. In the case of long-chain terminal olefin biphasic hydroformylation, a TPPTS/Rh ratio of 30 is enough to immobilize Rh in the aqueous phase and no leaching of Rh could be detected in the organic phase.^[19] Due to the strong chelated coordination of NBD, a higher molar ratio of TPPTS to Rh is required to efficiently immobilize Rh species in the aqueous phase. Therefore, a higher molar ratio of P/Rh = 50 is employed.

Recycling of catalyst in biphasic hydroformylation of NBD

This part of the study was aimed at investigating the facile recycling of the costly rhodium complex. The results in Table 4 indicate that the HRh(CO)(TPPTS)₃–TPPTS system can feasibly be used six times without sharp declines in conversion and selectivity. Since the separation of aqueous catalyst solution from products was handled in air, which easily caused the oxidation of TPPTS so losing the coordination ability with Rh, additional TPPTS is needed to keep the effective concentration of TPPTS to immobilize the catalyst in the aqueous phase. The results prove our hypothesis: 0.52 ppm (0.83%) of rhodium leaching into the organic phase is detected using ICP in the second run (Table 4, entry 2), but on adding a certain amount of ligand, the leaching concentration reduces to 0.14 ppm (0.22%), the conversion visibly increases from 47.7 to 49.4% (Table 4, entries 2 and 3) and the organic phase is colorless.

The further decrease of conversion might be attributed to the unavoidable loss of water and catalyst in the process of recycle manipulation, since the volume of aqueous phase itself was small.

Effect of cationic surfactants

Although a considerable yield can be achieved by prolonging the reaction time (Table 2, entry 7), the turnover frequency of the catalyst is still unimpressive. The addition of surfactant is admittedly

Table without	Table 4. Recycling of catalyst in biphasic hydroformylation of NBD without any additive					
Entry Conversion (%)		Selectivity (%)		Organic phase ^b	Rh (%) ^c	
		Monoaldehydes	Dialdehydes			
1	52.2	11.9	87.2	Colorless	0.13	
2	47.7	14.1	84.9	Slightly yellowish	0.83	
3 ^a	49.4	13.2	85.8	Colorless	0.22	
4 ^a	47.8	13.7	85.2	Colorless	0.19	
5 ^a	46.5	14.3	84.8	Colorless	0.16	
6 ^a	45.1	14.9	84.1	Colorless	0.14	
Peaction conditions are the same as in footnote of Table 1						

Reaction conditions are the same as in footnote of Table 1.

^a Adding half amount of the original ligand (TPPTS).

^b Color of upper organic phase.

^c Mass fraction of rhodium in the organic phase determined using ICP.

an economic and efficient method to improve the reaction rate in biphasic hydroformylation.^[19] Even though harsh reaction conditions could achieve the same ends, we still chose to try a surfactant in order to conduct the hydroformylation in a moderate reaction environment for the sake of practical applicability. To determine the effects of various cationic surfactants in the biphasic hydroformylation of NBD, single long-chain cationic surfactants and double long-chain cationic surfactants were investigated.

As evident from Table 5, compared with the blank experiment (entry 1), all the single long-chain cationic surfactants employed, DTAB, CTAB and DTAI, show a marked accelerating effect on the reaction rate at a concentration of 1 mmol I^{-1} . Additionally no obvious emulsion is observed after the reaction is completed, and the phase separation can be easily manipulated. The marked accelerating effects of the cationic surfactants may be attributed to the formation of ordered spherical micelles. Our previous work^[20,27] found that the micelles of the cationic surfactant can attract the negatively charged catalyst active species to the interface of the micelles through the electrostatic effect and increase the solubility of substrate in water by solubilization in the inner core of the micelles. Hence, the micelles have an advantage in breaking the mass transportation limitation, thus enhancing the reaction rate.

For a further understanding of the role of the cationic surfactant, the effects of single long-chain surfactants at various concentrations were investigated (Fig. 2). The results show that all of the conversions increase with an increase of the surfactant concentration, and so does the selectivity of dialdehydes. Also, although most of the substrate is converted into aldehydes when the concentration is 8.0 mmol I^{-1} , the system shows an apparent emulsification which complicates the decantation, and thus would passively hinder the separation of the two phases.

When comparing CTAB and DTAB, the former with a longer tail does not show a superior accelerating effect until the concentration reaches 2.0 mmol I^{-1} , then rapidly gives the highest conversion of 99.5% at 8.0 mmol I^{-1} . Unfortunately DTAI with the longest tail of 22 carbons does not exhibit the same excellent acceleration as CTAB and DTAB. This may suggest that a single long-chain surfactant with suitable hydrophobic tail has a better effect on the reaction rate, that is, a hydrophobic inner core composed of a shorter tail is favorable for the sterically demanding substrate NBD. To determine whether the steric hindrance of cationic surfactant has an impact on the biphasic hydroformylation of NBD, CPC, which has a pyridyl and an alkyl chain of 16 carbons, was investigated. The results (Fig. 2) suggest that CPC

Table 5. Effect of single long-chain cationic surfactants on biphasic hydroformylation of NBD						
Entry	Surfactant ^a	Conversion (%)	Selectivity (%)			
Monoaldehydes Dialdehyde						
1	b	51.7	12.8	86.0		
2	DTAB	79.9	9.3	89.9		
3	CTAB	68.7	11.1	87.9		
4	DTAI	61.2	17.3	81.2		
5	CPC	52.9	17.1	81.7		
Reaction conditions are the same as in footnote of Table 1 except for						

Reaction conditions are the same as in footnote of Table 1 except for the addition of surfactant.

^a Surfactant concentration = 1.0 mmol I^{-1} .

^b In the absence of any surfactant.



Figure 2. Influence of different kinds of single long-chain surfactants with various concentrations in the biphasic hydroformylation of NBD.

indeed shows an accelerating effect to some extent, but it is not as pronounced as that of CTAB. This is in agreement with our hypothesis that a suitable hydrophobic inner core microenvironment is beneficial to the reaction.

Since the single long-chain cationic surfactants show excellent accelerations, the double long-chain surfactants DDMAB, DCDAB and DCMAB were also employed in the biphasic hydroformylation of NBD. The results (Fig. 3) indicate that there is no obvious acceleration until the concentration markedly increases to 8 mmol I^{-1} . Also, all three give the highest conversions when the concentration reaches 20 mmol I^{-1} . Comparing the three double long-chain surfactants, and interestingly, DCDAB with two tails of 12 and 16 carbons performs better than DDMAB and DCMAB, which both have two equal-length tails.

Dilute double long-chain surfactant dissolved in aqueous solution usually forms a vesicle construct.^[23] The vesicle is a special bilayer membrane structure from the perspective of



Figure 3. Influence of different kinds of double long-chain surfactants with various concentrations in the biphasic hydroformylation of NBD.

Table 6. Recycling of biphasic hydroformylation of NBD in the presence
of cationic surfactants

Entry Conversion (%)		Selectivity (%)		Emulsification of system ^a	[Rh] (%) ⁶		
		Monoaldehydes Dialdehydes					
1	98.5	1.8	97.0	None	0.19		
2	91.1	10.8	88.5	Slight	14.17		
3	77.9	18.3	81.4	Serious	24.33		
^a Reaction conditions: [HRh(CO)(TPPTS) ₃] = 6.1×10^{-4} mol I ⁻¹ in 2 ml of H ₂ O, [TPPTS]/[Rh] = 50 (molar ratio), NBD = 0.5 ml (4.9 mmol), [CTAB] = 7.0 mmol I ⁻¹ , toluene 1.5 mL, 70 °C, 2.0 MPa, 120 min. ^b Mass fraction of rhodium in the organic phase determined using ICP.							

microenvironment, which is totally different from a micelle. The structure, on the one hand, has a tremendously increased interfacial area and attracts more catalytic active species via its larger internal and external aqueous phases; on the other hand, the increased quantity of bilayer alkyl chains form a more compact hydrophobic region which hardly suits the shift of NBD to the interfacial area. Thus, the sterically hindered NBD would with difficultly contact the catalytic active species on the surface of bilayer membrane and the acceleration is not clear. The biphasic hydroformylation of dicyclopentadiene showed the same trend.^[28]

Furthermore, we suppose that with an increase in concentration, the structure of the vesicle might change a lot. High concentration could possibly cause a sequence of variations in the regular oblate bilayer membrane and the hydrophobic region would be less crowded, which makes the movement of NBD easier, thus increasing the conversion.

Recycling in presence of surfactants

Finally, catalytic recycling experiments in the presence of surfactants were conducted. Although an excellent substrate conversion is achieved (Table 6), the recycle times are less impressive. Moreover, the system shows emulsification in the process and ICP analysis detects a loss of Rh metal, which is detrimental for the separation of the aqueous phase from the organic phase and the Rh loss is unexpected.

Conclusions

The hydroformylation of NBD catalyzed by HRh(CO)(TPPTS)₃–TPPTS was systematically studied for the first time. Under mild conditions, the hydroformylation proceeded better in the biphasic system than in the homogeneous system. The results of the recycling of the catalyst without surfactants showed great stability of the catalyst and proved its application potential. Cationic surfactants could effectively accelerate the reaction rate of NBD hydroformylation in the biphasic system. This confirmed the acceleration mechanism of cationic surfactants that our group previously put forward. However, the presence of cationic surfactants was detrimental to the reuse of the catalyst in this system. Determination of the reason requires further study.

Acknowledgments

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