

Hydroformylation of 1-hexene catalyzed by water soluble $\text{CoCl}_2(\text{TPPTS})_2$ in biphasic medium

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Abstract

$\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-hexene was studied in an aqueous biphasic medium. The effect of temperature, pressure, and concentration of cobalt catalyst on the reaction was studied. At elevated temperatures and pressures, it gave >90% conversion with 68% selectivity for aldehyde and *n/iso* ratio of 3.0 for the aldehyde.

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1. Introduction

Hydroformylation, the addition of CO and H₂ to alkenes, is one of the most important syn-gas related reactions, which uses the largest volume of syn-gas in homogeneously catalyzed reactions [1]. The resultant aldehydes are versatile chemical intermediates that can be easily converted to a variety of industrially important secondary products [2]. The most valuable industrial applications of hydroformylation are the manufacture of propanal and n-butanal from ethylene and propylene, respectively, and the synthesis of long chain alcohols from olefins such as 1-octene and higher ones [3]. For the Cobalt based systems, the hydroformylation of olefins to aldehyde or alcohol largely depends upon the reaction temperature. The aldehyde formation is favored by low temperature whereas alcohol is favored if the reaction temperature is above 160 °C [4,5]. The hydroformylation reaction was first discovered on a heterogeneous Fischer–Tropsch (F–T) cobalt catalyst [6] wherein it was recognized that cobalt carbonyls generated from the heterogeneous cobalt metal during the reaction were responsible

for the catalysis [1,7–9]. Majority of olefin hydroformylation processes are using cobalt complexes as a catalyst, however, during last decades, the rhodium complexes are also being increasingly used [10]. This is mainly due to milder conditions of temperature and pressure, high conversion rates of alkenes and high selectivity to n-aldehydes [11] in the case of rhodium based catalysts. Particularly, phosphine-modified rhodium catalysts find wide application in propylene hydroformylation [12]. However, cobalt is preferable over rhodium as a hydroformylation catalyst for the higher olefin [13]. Due to the high cost of rhodium, efforts have been devoted to improve rhodium recovery after the completion of reaction [10]. At the same time, research is still directed to study and exploit (a) in-expensive metals like ruthenium and cobalt as they are known to be highly active for F–T synthesis [14–19]; (b) easy separation and re-use of the catalyst. For example, water soluble catalysts in biphasic media have been applied in the Rhone–Poulenc oxo process [20–22] for the hydroformylation of propylene. The biphasic fluoros catalysts [23–25], immobilizing catalysts via the sol–gel process [26], anchoring on to a polymer matrix [27–31], or encapsulation in micro/mesoporous materials [25,32] have been investigated for the hydroformylation of various olefins. The common incentive of all these approaches is to improve the catalyst recovery and recycling. Recently Davis et al. [33] have used phosphine-modified cobalt carbonyls complex, $\text{Co}_2(\text{CO})_6(\text{TPPTS})_2$, in a biphasic

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media for the hydroformylation of olefins. The catalytic active intermediates may be the $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_3\text{L}$. The $\text{HCo}(\text{CO})_4$ species is water insoluble and more reactive than water soluble $\text{HCo}(\text{CO})_3\text{L}$ species.

Beller et al. have combined the concept of ligand modification with the technique of two-phase catalysis by using water soluble Co-TPPTS complex [34] and reported high reaction rates and *n/iso* selectivities for the hydroformylation of internal olefins, 3-pentene. Temperatures were in the range of 100–190 °C with pressures between 80 and 100 bar. In order to ensure solubility between the aqueous and the organic phase, co-solvent (1-butanol) was added.

Here, we report, $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-hexene with varying temperature, pressure, and catalyst concentration and found that $\text{CoCl}_2(\text{TPPTS})_2$ is more efficient than $\text{RuCl}_2(\text{TPPTS})_3$ as a hydroformylation catalyst. Water soluble TPPTS complex of ruthenium, $\text{RuCl}_2(\text{TPPTS})_3$, and PPh_3 complex of ruthenium, $\text{RuCl}_2(\text{PPh}_3)_3$ were found to have low hydroformylation activity as well as high isomerization and hydrogenation activity [35–37]. Low hydroformylation and high hydrogenation activity was attributed to the formation of intermediate compound, $\text{HRuCl}(\text{CO})(\text{phosphine})_2$, which is more active toward the hydrogenation of olefins.

2. Experimental

2.1. Materials

The trisodium salt of tri(*m*-sulfophenyl)-phosphine (TPPTS) was prepared in accordance with method described in the literature [38]. The syn-gas (99.8%) used was from Hydro Gas India Pvt. Ltd., India. 1-Hexene and hydrocarbons used were from Aldrich Chemicals, USA. The sodium salt of TPPTS oxide as an impurity was less than 5% and water content was less than 10%. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in reaction was purchased from Merck, India.

2.2. Instrumentation

All the reactions were performed in 100 ml autoclave (Autoclave Engineers, USA). NMR measurements were done on Bruker advance DPX 200 MHz FT-NMR and IR spectra have been recorded on Perkin-Elmer spectrum GX FT-IR system and CHN analysis has been done on Perkin-Elmer C, H, N, S and O analyzer. Products were analyzed with SHIMADZU GC-17A gas chromatograph (GC) using flame ionization detector (FID) having 5% diphenyl and 95% dimethylsiloxane capillary column (60 m length, 0.25 mm diameter). Column temperature was kept initially at 40 °C for 5 min and then raised to 150 °C at the heating rate of 10 °C/min. Nitrogen was used as a carrier gas (1.2 ml/min). *n*-Decane was used as internal standard and the GC was standardized using known amount of heptanal.

2.3. Synthesis

Water soluble cobalt complex, $\text{CoCl}_2(\text{TPPTS})_2$, was prepared following the procedure reported by Cotton et al. [39] for the synthesis of $\text{CoCl}_2(\text{PPh}_3)_2$. One hundred milligram of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was taken in 7 ml of ethanol to which 500 mg of TPPTS dissolved in water was added and solution was stirred under reflux for 3 h. The volume of the reaction mixture was reduced to minimum and cold acetone was added to precipitate the complex. The complex was filtered and washed with cold acetone and finally re-crystallized from water:acetone mixture.

2.4. Catalytic reaction

One millimole of catalyst, $\text{CoCl}_2(\text{TPPTS})_2$, dissolved in 25 ml water and 3 g of substrate was taken in stainless steel autoclave reactor. The reactor was flushed with nitrogen three times followed by flushing syn-gas twice at room temperature after which reactor was brought to reaction temperature and pressurized with desired syn-gas pressure. The reaction was initiated by stirring and after desired reaction time, the stirring was stopped and reactor was cooled over night. Separating funnel was used to separate reaction mixture and organic layer was analyzed on GC.

3. Results and discussion

3.1. Synthesis and characterization

TPPTS was characterized by physicochemical techniques. The C, H, N analytical data obtained for Cobalt (II) complex $\text{CoCl}_2(\text{TPPTS})_2$ is as: calc. (found) C: 34.15 (34.75); H: 1.89 (1.93). ^{31}P NMR spectra of the isolated complex gave a broad singlet at 53.6 ppm indicating that two phosphorous of TPPTS are equivalent. The broad singlet may be due to the fast exchange due to the paramagnetic nature of the complex. However, the chances that two phosphorous donor atoms being non-equivalent is very remote for the square planer/tetrahedral complex, $\text{CoCl}_2(\text{TPPTS})_2$. IR spectra of the isolated complex gave band at 1191 and 1106 cm^{-1} due to the sulfonation of phenyl ring of PPh_3 .

The catalytic hydroformylation of 1-hexene was studied at 60–120 °C temperature and constant pressure of 9 MPa as cobalt-catalyzed process is high-pressure process and the results obtained are shown in Table 1. An increase in the conversion of 1-hexene to the various products was observed with the increase in the temperature. The yield of aldehyde decreases from 83 to 68% with an increase in the isomerization and hydrogenation reaction when the temperature increases from 60 to 100 °C. However, at 120 °C, there is an increase in the isomerization of 1-hexene to 2-hexene/3-hexene along with the decrease in the hydrogenation activity whereas the hydroformylation activity remains the same. This may be due to the lower activity of

Table 1

Effect of temperature on the hydroformylation of 1-hexene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$ in aqueous medium^a

Temperature (°C)	Pressure, (MPa)	Conversion (%)	Selectivity (%)			
			<i>n</i> -Hexane	2-Hexene and 3-hexene	Aldehyde	<i>n</i> / <i>i</i>
60	9	63	7	10	83	2.2
80	9	69	12	18	70	3.4
100	9	87	17	15	68	2.8
120	9	87	8	23	69	2.9
100	7	76	19	14	67	3.1
100	5	62	48	14	41	2.8
80 ^b	6	30	3	2	95	3.1

^a Reaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 1 \text{ mmol}$; substrate = 23.04 mmol; decane: 0.5 ml; solvent (water) = 25 ml; and reaction time = 7 h.^b $[\text{CoCl}_2(\text{PPh}_3)_2] = 0.1 \text{ mmol}$; 1-hexene = 23.04 mmol; $P_{\text{syn-gas}} = 6 \text{ MPa}$; $\text{CO} : \text{H}_2 = 1 : 1$; solvent (acetonitrile) = 25 ml; reaction time = 7 h.

the complex for the hydrogenation of internal olefin and increase in the isomerization activity at 120 °C. This was confirmed by studying the hydroformylation of *trans*-4-octene under the similar reaction conditions, wherein neither hydroformylated nor hydrogenated product was observed. There is slight increase in the *n*/*i* ratio for aldehyde as we increase the temperature from 60 to 120 °C. There was no formation of alcohol under the employed reaction conditions for the hydroformylation of 1-hexene using $\text{CoCl}_2(\text{TPPTS})_2$ as a catalyst. It is reported that aldehyde formation is favored at low temperature, whereas an increase in temperature above 160 °C greatly facilitates hydrogenation of aldehyde to alcohol [4,5]. As we have studied the title reaction below 120 °C, it favors the formation of heptanal rather than heptanol.

The catalytic activity of $\text{CoCl}_2(\text{TPPTS})_2$ towards the hydroformylation of 1-hexene was studied at different pressures at 100 °C and results are given in Table 1. At low syn-gas pressure of 5 MPa, it gave 48% hydrogenated product and 41% hydroformylated product. This may be due to the low concentration of CO gas at low syn-gas pressure, which may not be sufficient to form cobalt-carbonyl complex, which is an active intermediate for the hydroformylation reaction. As the pressure increases from 5 to 7 MPa, the selectivity towards aldehyde increases from 41 to 67% with an increase in conversion of 1-hexene from 61 to 76%. Further increase in pressure to 9 MPa increases the conversion of 1-hexene, however, the selectivity towards aldehyde (68%) remains the same. The *n*/*i* ratio for the aldehyde is not much affected with the increase in pressure from 5 to 9 MPa. Generally, there is a decrease in the *n*/*i* ratio with the increase in the reaction temperature due to increase in the isomerization reaction.

Table 2

Effect of catalyst concentration on the hydroformylation of 1-hexene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$ in aqueous medium^a

Catalyst concentration (mmol)	Conversion (%)	Selectivity (%)				<i>n</i> / <i>i</i>
		<i>n</i> -Hexane	2-Hexene and 3-hexene	Aldehyde	Alcohol	
1.00	87	17	15	68	–	2.8
0.50	92	21	10	69	–	2.7
0.25	94	24	11	65	–	2.2

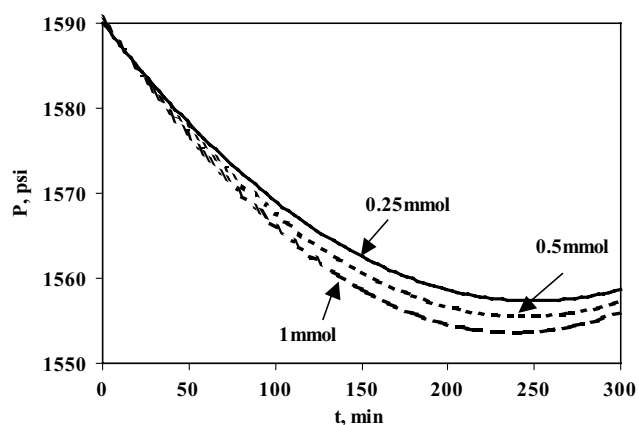
^a Reaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 0.25 \text{ to } 1 \text{ mmol}$; substrate = 23.04 mmol; decane: 0.5 ml; solvent (water) = 25 ml; $T = 100 \text{ °C}$; $P_{\text{syn-gas}} = 9 \text{ MPa}$; and reaction time = 7 h.

Fig. 1. The plot of pressure drops with time for the hydroformylation of 1-hexene under different catalyst concentration: $[\text{CoCl}_2(\text{TPPTS})_2] = 0.25\text{--}1 \text{ mmol}$; substrate = 23.04 mmol; decane: 0.5 ml; solvent (water) = 25 ml; $T = 100 \text{ °C}$; and reaction time = 7 h.

In order to study the effect of catalyst concentration, catalyst concentration was varied from 1.0 to 0.25 mmol under the optimum reaction conditions of 100 °C temperature, 9 MPa of syn-gas pressure and the reaction time of 7 h. The results are given in Table 2. It can be seen from these results that after 7 h of reaction time, the conversion of olefin does not vary significantly with catalyst concentration.

In order to verify the above results, we have studied the drop in pressure with time for the hydroformylation of 1-hexene under different $\text{CoCl}_2(\text{TPPTS})_2$ concentration and the results are given in Fig. 1. From these results it is evident that at 1 mmol $\text{CoCl}_2(\text{TPPTS})_2$ concentration, more than 95% reaction is over within 3 h whereas

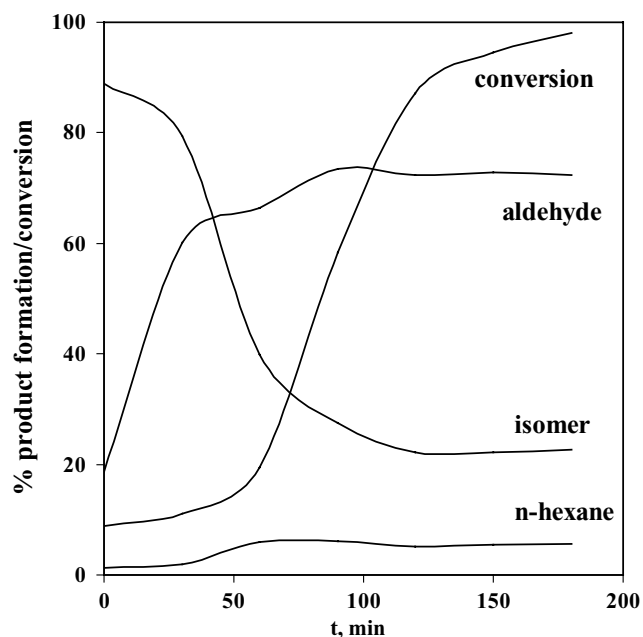


Fig. 2. The evolution of product with time for the hydroformylation of hex-1-ene using 1 mmol Co-TPPTS complex as catalyst at 9 MPa pressure and 100 °C temperature.

when the $\text{CoCl}_2(\text{TPPTS})_2$ concentration was decreased to 0.025 mmol., it took more than 5 h for the completion of reaction, which clearly reveals that with the increase in the cobalt concentration, there is an increase in the reaction rate and the reaction take less time for completion when the cobalt concentration is increased.

We have also investigated evolution of product formation with time for the hydroformylation of 1-hexene using Co-TPPTS complex as a catalyst at 9 MPa pressure and 100 °C temperature (Fig. 2). In the initial stage of the reaction, isomerization of 1-hexene dominates, however, as the reaction proceed, formation of aldehyde increases with the decrease in the isomerization reaction.

The result as shown in Tables 1 and 2 indicate that for $\text{CoCl}_2(\text{TPPTS})_2$, optimum reaction conditions are 100 °C temperature with 8–9 MPa pressures. The amount of catalyst present between the organic and aqueous phase plays an important role for hydroformylation reaction because in biphasic medium reaction mainly occur in the interphase and the excess amount of catalyst may not alter the activity. This is further supported by the data obtained from the hydroformylation of 1-hexene done in organic medium using $\text{CoCl}_2(\text{PPh}_3)_2$ as a catalyst, wherein the conversion of 1-hexene is substantially lower than the conversion observed using water soluble catalyst under the similar reaction conditions (Table 1). The catalytic active intermediate for water soluble catalyst may be the $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_3\text{L}$. The $\text{HCo}(\text{CO})_4$ species is water insoluble and more reactive than water soluble $\text{HCo}(\text{CO})_3\text{L}$ species. The IR spectra of the aqueous reaction mixture gave a broad and strong IR peak at 2060 cm^{-1} in

whereas the reported IR peak for $\text{HCo}(\text{CO})_3(\text{Bu}_3\text{P})$ is at 2049 cm^{-1} .

An important feature of the water soluble catalysts system is the re-use of the catalyst. The efficiency of the catalyst recycling system was determined by reusing the aqueous phase of the reaction mixture for further carrying out the hydroformylation reaction wherein 65% conversion of olefin was obtained with 70% aldehyde selectivity with 2% leaching of cobalt in the organic phase. The second recycling experiment results in further drop in the conversion to 60%. This can be attributed to the leaching of cobalt in the organic phase in the first two catalytic run and also increase in the sulphonated phosphine in the aqueous phase, which may decrease the hydroformylation rate [40].

4. Conclusion

$\text{CoCl}_2(\text{TPPTS})_2$ was found to be effective catalyst for hydroformylation of 1-hexene at 100 °C temperature and 9 MPa pressure. It was also observed that under optimum reaction conditions employed, the catalyst selectively gave only aldehyde. The aldehyde formation is favored by low temperature, whereas an increase in temperature above 160 °C greatly facilitates hydrogenation of aldehyde to alcohol. Generally cobalt system is high temperature process, but in present system, after modifying the cobalt complex, we are able to get the hydroformylated product under milder reaction conditions.

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