

CoCl₂(TPPTS)₂ catalyzed hydroformylation of 1-octene and 1-decene in the presence of surfactant and co-solvents in a biphasic medium

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Abstract

CoCl₂(TPPTS)₂ catalyzed hydroformylation of 1-octene and 1-decene was studied in an aqueous biphasic medium. The effect of temperature, pressure and addition of cetyltrimethylammonium bromide (CTAB) and tri(*m*-sulfophenyl)-phosphine (TPPTS) in the reaction mixture on the hydroformylation of alkenes was investigated. Increase in conversion of 1-octene and 1-decene with higher aldehyde selectivity was observed in the presence of CTAB. The leaching of cobalt complex, CoCl₂(TPPTS)₂, from aqueous phase to organic phase in presence of TPPTS was observed to decrease. There was slight decrease in the conversion on increasing the TPPTS to cobalt molar ratio. The addition of CTAB increases the conversion (95%) and selectivity (90–95%) for aldehyde whereas the addition of TPPTS facilitates the separation of organic–aqueous phase. Hydroformylation was also studied in the presence of ethanol and methanol under the optimum reaction conditions.
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1. Introduction

Aqueous biphasic catalytic systems have opened a new perspective for transition metal complexes driven homogeneous catalysis particularly after the industrial success of propene hydroformylation catalyzed by water-soluble HRh(CO)–(TPPTS)₃ [TPPTS: P(*m*-C₆H₄SO₃Na)₃], developed by Rhône-Poulenc and Ruhr-Chemie [1]. Indeed, lower olefins such as ethylene, propene and butene have solubility high enough to assure chemical reaction without mass-transfer limitations [2,3] in the aqueous catalytic phase. In contrast, the solubility of olefins with five or more carbon atoms is too low for industrially viable rates to be achieved and the presence of co-solvent [4–8], surfactant [4,9–18], amphiphilic ligands [19–25] or cyclodextrins [26–31] is required.

Hydroformylation of long-chain alkenes has been largely studied using cobalt carbonyl complexes. Furthermore, due to higher cost of rhodium complexes, it is imperative to search

for less expensive metals like ruthenium and cobalt which are known to be highly active catalysts [32–35] for many reactions. Recently, we have reported the hydroformylation of 1-hexene catalyzed by CoCl₂(TPPTS)₂ [36] and have shown good activity and selectivity towards heptaldehyde formation. In continuation, we are reporting here the hydroformylation of 1-octene and 1-decene using CoCl₂(TPPTS)₂ as a catalyst in the presence of added surfactant and water miscible solvents. Increase in aldehyde formation was observed with an increase in surfactant concentration. However, the conversion obtained with cobalt complex was lower compared to those obtained with rhodium metal complex [36].

2. Experimental

2.1. Materials

The trisodium salt of tri(*m*-sulfophenyl)-phosphine (TPPTS) was prepared in accordance with method described in the literature [12,37]. The syngas (99.8%) used was from Hydro Gas India Pvt. Ltd., India. 1-octene and 1-decene used were from M/s. Aldrich Chemicals, USA. The sodium salt of tri(*m*-sulfophenyl) phosphine oxide as an impurity was less than 5%

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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. Ethanol, methanol and cetyltrimethylammonium bromide (CTAB) were from s.d. Fine Chemicals, India.

Water-soluble cobalt complex, $\text{CoCl}_2(\text{TPPTS})_2$, was synthesized following the procedure reported by Cotton et al. [38] for the synthesis of $\text{CoCl}_2(\text{PPh}_3)_2$.

2.2. Instrumentation

All the reactions were performed in 100 ml autoclave (Autoclave Engineers, EZE-Seal Reactor, USA). ^{31}P NMR measurements were done using D_2O as solvent and 85% H_3PO_4 as an internal reference, on Bruker Avance DPX 200 MHz FT-NMR. IR spectra were recorded using nujol mull and KBr pellet on PerkinElmer spectrum GX FT-IR system in the range $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . CHN analysis has been done on PerkinElmer, 2400 C, H, N, S/O analyzer. Atomic Absorption Spectra were recorded using Shimadzu AA-680/G V-5 Spectrometer. 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 initially kept at $40\text{ }^\circ\text{C}$ for 5 min and then raised to $200\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$. Nitrogen was used as a carrier gas ($1.2\text{ ml}/\text{min}$). *n*-decane and *n*-tridecane were used as internal standards and the GC was also calibrated using known amount of nonanal and undecanal.

2.3. Catalytic reaction

1 mmol/l catalyst, $\text{CoCl}_2(\text{TPPTS})_2$, in 25 ml water and 2 g substrate were taken in a stainless steel autoclave 100 ml reactor. The reactor was flushed with nitrogen three times followed

by twice flushing with syngas at room temperature after which reactor was brought to reaction temperature and pressurized with syngas to desired pressure. The reaction was initiated by stirring and after set reaction time, the stirring was stopped and reactor was cooled by circulating cold water in the cooling coil. Separating funnel was used to separate reaction mixture and organic layer was analyzed by GC.

3. Results and discussion

3.1. Catalytic study

TPPTS was characterized by physicochemical techniques. The C, H, N analytical data obtained for cobalt(II) complex $\text{CoCl}_2(\text{TPPTS})_2$ are as: calc. (found) C: 34.15 (34.45); H: 1.89 (1.86). ^{31}P NMR spectrum of the isolated complex gave a broad singlet at 54 ppm (due to the paramagnetic nature of the complex) indicating the equivalence of two phosphorous atoms of TPPTS. IR spectrum of the isolated complex gave band at 1191 and 1106 cm^{-1} due the sulfonation of phenyl ring of PPh_3 .

The catalytic hydroformylation reaction of 1-octene and 1-decene was performed at varied temperature and pressure for determining the optimum conditions to get corresponding hydroformylated products. The alkene conversion and aldehyde selectivity data for $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene performed at $60\text{--}120\text{ }^\circ\text{C}$ temperature and 8 MPa pressure are given in Table 1. The conversion of alkenes increases with an increase in the reaction temperature. However, selectivity for hydroformylated product is found to decrease with increasing temperature. For example, at $60\text{ }^\circ\text{C}$, 1-octene conversion is only 9% but selectivity towards the nonanal was 87%. At $120\text{ }^\circ\text{C}$, alkene conversion increased up to 73% with nonanal selectivity decreasing to 38%. The alkene conversion

Table 1
Effect of temperature and pressure on hydroformylation of 1-octene and 1-decene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$ in aqueous medium

Temperature ($^\circ\text{C}$)	Pressure (MPa)	Conversion (%)	Selectivity (%) for 1-octene hydroformylation			
			1-octene	<i>n</i> -octane	2- and 3-octene	Aldehyde
60	8	9	9	4	87	2.1
80	8	14	7	16	77	2.7
100	8	28	10	26	64	2.8
120	8	73	10	52	38	2.7
100	5	24	11	44	55	2.9
100	7	28	10	27	63	2.8
100	9	29	10	25	65	3.0
Temperature ($^\circ\text{C}$)	Pressure (MPa)	Conversion (%)	Selectivity (%) for 1-decene hydroformylation			
			1-decene	<i>n</i> -decane	2- and 3-decene	Aldehyde
60	8	11	6	20	74	2.0
80	8	18	6	29	65	2.5
100	8	31	5	38	57	2.7
120	8	75	5	68	27	2.4
100	5	26	8	50	42	2.7
100	7	29	6	46	48	2.6
100	9	33	6	41	53	2.7

Reaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 1.0\text{ mmol}/\text{l}$; substrate/cat = 700; decane: 0.5 ml; solvent (water) = 25 ml; reaction time = 5 h.

Table 2
 $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-decene^a and 1-octene^b

CTAB concentration (mmol/l)	Conversion (%)	Selectivity (%)			<i>n/i</i> ratio	Org/aqu phase sep. time (min)
		<i>n</i> -decane	2- and 3-decene	Aldehyde		
2.5	69	6	16	78	2.6	15
5.0	89	2	5	93	2.5	30
5.5	96	1	7	92	2.3	60
5.5 ^b	95	2	3	95	2.3	60

^a Reaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 1.0$ mmol/l; substrate/cat = 700; solvent (water) = 25 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

^b Data for $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene in presence of 0.5 mmol/l CTAB: $[\text{CoCl}_2(\text{TPPTS})_2] = 1.0$ mmol/l; substrate/cat = 700; solvent (water) = 25 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

and nonanal selectivity for 1-octene at 100 °C are comparable to the values obtained with rhodium system [39]. 1-decene hydroformylation reaction follows similar trend. At 8 MPa syngas pressure, with the increase in temperature from 60 to 120 °C, 1-decene conversion increases from 11 to 75%, however, the selectivity for aldehyde decreases from 74 to 27%. The decrease in aldehyde selectivity at higher temperatures is mainly due to enhanced isomerization of alkenes as is also seen from the selectivity data for isomerized alkenes given in Table 1 (observed by GCMS analysis). The hydroformylation activity of the isomerized alkenes is less due to their low solubility in the aqueous phase resulting into lower aldehyde selectivity at higher temperatures [40,41].

The catalytic hydroformylation reaction of cobalt system was studied at 100 °C at different syngas pressure (Table 1). At 5 MPa pressure, alkene isomerized product and hydroformylated product for 1-octene were found to be 43 and 55%, respectively (50 and 42% for 1-decene), whereas hydrogenation of 1-octene is 10–11% (6–8% for 1-decene) at different applied pressure. With increase in pressure from 5 to 9 MPa, selectivity for hydroformylated product is observed to increase for nonanal (from 55 to 63%) and undecanal (from 42 to 53%). Increased formation of aldehydes at higher pressure could be due to enhanced availability of carbon monoxide and hydrogen at higher pressure. The

solubility of carbon monoxide in water at 100 °C and at 5 MPa is 3.8 mmol/l and at 9 MPa is 6.8 mmol/l, respectively [42].

3.2. Effect of CTAB and TPPTS on the $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene

The purpose of using biphasic catalyst system is to have easy recycling of the catalyst and separation of oxo product. The main drawback of the water-soluble catalyst system is the low solubility of the 1-octene and 1-decene in aqueous media. The solubility of the alkenes can be enhanced by increasing the interface area between the aqueous and non-aqueous layer. This can be achieved by adding surfactant to the reaction solution. Li et al. [41] had reported that the addition of a cationic surfactant such as CTAB greatly accelerates the $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ catalyzed hydroformylation of long chain olefins and have used CTAB concentration in the range of 1×10^{-3} to 5×10^{-3} mol/l. Both conversion of alkenes and selectivity towards the aldehydes for the $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of alkenes show significant improvement (Table 2) in the presence of CTAB. This could be explained in terms of increased interlayer area which brings catalyst and reactant molecules in proximity to react. It is further observed (Table 2 and Fig. 1) that the separation of organic and aqueous phases after the comple-

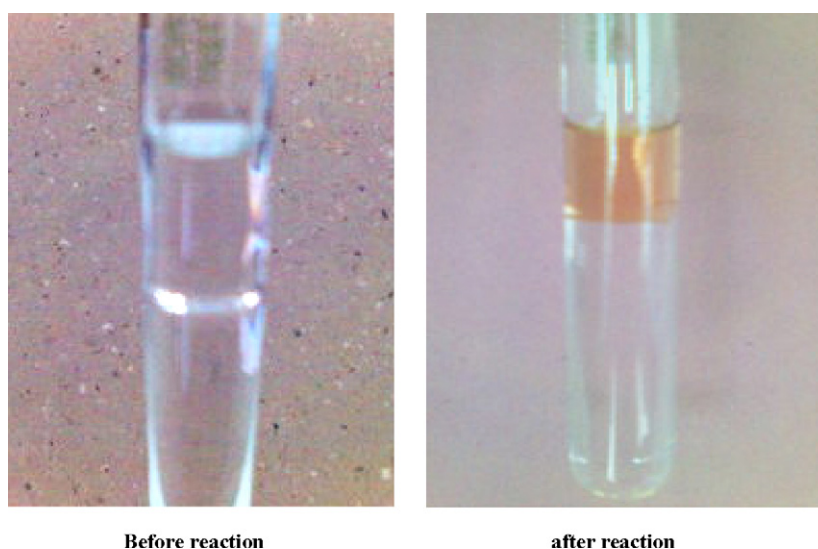


Fig. 1. Layer separation before and after the $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-decene: reaction conditions: substrate/cat = 700; [CTAB] = 5.5 mmol/l; solvent (water) = 25 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

Table 3
Effect of molar ratio of TPPTS to catalyst on $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene

TPPTS/Co (mole ratio)	Conversion (%)	Selectivity (%)				Cobalt leaching (ppm)
		1-octene	<i>n</i> -octane	2- and 3-octene	Aldehyde	
1	28	8	29	63	2.8	1.0
2	27	9	24	67	3.0	0.1
4	25	9	25	66	2.9	0.06
8	21	5	24	71	3.2	0.00

TPPTS/Co (mole ratio)	Conversion (%)	Selectivity (%)				Cobalt leaching (ppm)
		1-decene	<i>n</i> -decane	2- and 3-decene	Aldehyde	
1	31	5	36	59	2.7	1.0
2	29	6	32	62	2.8	0.1
4	28	5	32	63	3.0	0.05
8	25	6	28	67	3.3	0.00

Reaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 1 \text{ mmol/l}$; substrate/cat = 700; decane: 0.5 ml; solvent (water) = 25 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

tion of reaction occurs within an hour that helps to recover and recycle the catalysts and products from the reaction medium.

The effect of addition of TPPTS under the optimized reaction conditions (8 MPa syngas pressure and 100 °C reaction temperature with 1 mmol/l catalyst concentration) for the $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene was also studied. $\text{CoCl}_2(\text{TPPTS})_2$ to TPPTS molar concentration was varied from 1:1 to 1:8. The data (Table 3) show that with increase in TPPTS concentration (TPPTS to catalyst molar ratio of 1:1 to 1:8), there is a decrease in the 1-octene conversion from 28 to 21% (1-decene conversion decreases from 31 to 26%) with 3–8% increase in the aldehyde selectivity. The decrease in conversion could be due to the enhanced stability of the active catalytic species with the increase of TPPTS concentration. The leaching of cobalt from aqueous phase to the organic phase decreases drastically with the increase in TPPTS concentration (Table 3) without compromising with the conversion and selectivity. This is very significant as one of the prerequisite of water-soluble catalysts is the efficient re-use of the aqueous catalyst phase and minimal loss of metal in the reaction products.

3.3. Effect of solvents on the $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene

In order to overcome the problem of low solubility of 1-decene and 1-octene in aqueous medium during hydroformy-

lation reaction, use of water miscible solvent such as methanol and ethanol was attempted (Table 4). 1-decene conversion of 51 and 54% was observed with aldehyde selectivity of 75 and 77% in methanol and ethanol, respectively. When ethanol was used as solvent, selectivity towards hydroformylated product was 77%, with 4% hydrogenated and 19% isomerized product, while in methanol selectivity towards hydroformylated product was only 75% and more hydrogenated (4%) and isomerization (21%) products were obtained. In the case of 1-octene hydroformylation, 1-octene conversion is 55% with 80% selectivity for aldehyde in both methanol and ethanol.

The alcoholic solvents could have several types of effects operating at the same time during the reaction. They could take part in the catalytic cycle by coordination to the cobalt center. Through electronic effect, the coordinated solvents might inhibit the dissociation of CO over the cobalt center and make it more active for the insertion to Co–olefin bond. The proton and hydrogen binding of the solvents might also have effect on the reaction.

3.4. Effect of catalyst concentration on $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene

The effect of catalyst concentration (0.25–1.0 mmol/l) on 1-decene and 1-octene conversion studied at 100 °C and 8 MPa pressure show conversion to increase from 22 to 31% for 1-decene (21–28% for 1-octene) with aldehyde selectivity

Table 4
Effect of co-solvents on the hydroformylation of 1-octene and 1-decene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$ in aqueous medium

Substrate	Co-solvent	Conversion (%)	Selectivity (%)				<i>n/i</i> ratio
			<i>n</i> -Alkane	2-Alkene	3-Alkene	Aldehyde	
1-octene	Methanol	53	6	12	2	80	2.6
	Ethanol	55	5	11	2	82	2.5
1-decene	Methanol	51	4	13	8	75	2.4
	Ethanol	54	4	12	7	77	2.3

^aReaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 1.0 \text{ mmol/l}$; substrate/cat = 700; water = 25 ml; co-solvent = 10 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

Table 5

Effect of catalyst concentration on hydroformylation of 1-octene and 1-decene catalyzed by $[\text{CoCl}_2(\text{TPPTS})_2]$ in aqueous medium

Catalyst concentration (mmol/l)	Conversion (%)	Selectivity (%)				<i>n/i</i> ratio
		1-decene	<i>n</i> -decane	2-decene	3-decene	
1.00	31	5	27	11	57	2.7
0.50	26	6	28	12	54	2.6
0.25	22	8	28	14	50	2.4

Catalyst concentration (mmol/l)	Conversion (%)	Selectivity (%)				<i>n/i</i> ratio
		1-octene	<i>n</i> -octane	2-octene	3-octene	
1.00	28	10	21	5	64	2.8
0.50	24	12	21	5	62	2.6
0.25	21	15	22	7	56	2.5

Reaction conditions: $[\text{CoCl}_2(\text{TPPTS})_2] = 0.25\text{--}1.00$ mmol/l; substrate/cat = 700; decane: 0.5 ml; solvent (water) = 25 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

increasing from 50 to 57% for 1-decene and from 56 to 64% for 1-octene (Table 5).

3.5. Effect of TPPTS in the presence of CTAB for $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene

The effect of simultaneous addition of CTAB and TPPTS was also studied for the hydroformylation of 1-octene and 1-decene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$. The TPPTS concentration was varied from 0 to 16 mmol/l (TPPTS/catalyst ratio) in the presence of 5.5×10^{-3} mol/l of CTAB. Under these conditions, the conversion of alkenes increased to 95% with the selectivity of aldehyde increasing to 90–95% and separation of organic–aqueous phase is facilitated due to the salting effect of TPPTS (Table 6).

The addition of TPPTS helps in rapid separation of aqueous and organic phases after the completion of the reaction whereas CTAB helps to increase the conversion and selectivity.

3.6. Recycling of the catalyst

The recycling of cobalt–TPPTS catalyst for 1-decene and 1-octene hydroformylation was studied up to four cycles in

the presence of 16 mmol/l of TPPTS and 5.5 mmol/l of CTAB. The data given in Table 7 show that alkenes conversion (95%) is retained even after four cycles with aldehyde selectivity in the range of 87–90%. After the reaction, the reaction mixture displays three layers; upper organic layer is almost colorless, interfacial emulsion layer is brown and bottom aqueous layer is yellow. The recycling experiments using the solution containing both middle interfacial layer and aqueous layer in successive reactions show that the activity does not decrease noticeably. This confirmed that the leaching of cobalt from aqueous phase to organic phase is extremely low. If only the aqueous phase is used for the consequent reaction, 1-decene conversion decreases notably from 90 to 53%. Similar phenomenon was also reported for Rh/TPPTS/CTAB system [43].

3.7. Reaction mechanism

Based on the literature data and experimental observation, a reaction scheme is proposed for the formation of active catalytic species $\text{HCo}^I(\text{CO})_3(\text{TPPTS})$ for the catalytic hydroformylation of olefins (Schemes 1 and 2). $\text{CoCl}_2(\text{TPPTS})_2$ reacts with carbon monoxide to give five coordinated, $\text{Co}(\text{CO})(\text{TPPTS})_2\text{Cl}_2$ (1) and six coordinated $\text{Co}(\text{CO})_2(\text{TPPTS})_2\text{Cl}_2$ (2) cobalt carbonyl complexes, which are in equilibrium. The formation

Table 6

Effect of TPPTS to catalyst ratio in the presence of CTAB on the $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-decene and 1-octene

TPPTS/cat (mmol)	Conversion (%)	Selectivity (%)			<i>n/i</i> ratio	Org/aqueous phase separation time (min)
		1-decene	<i>n</i> -decane	2- and 3-decene		
0	96	1	7	92	2.3	60
10	95	1	4	95	2.3	15
16	95	2	8	90	2.3	5

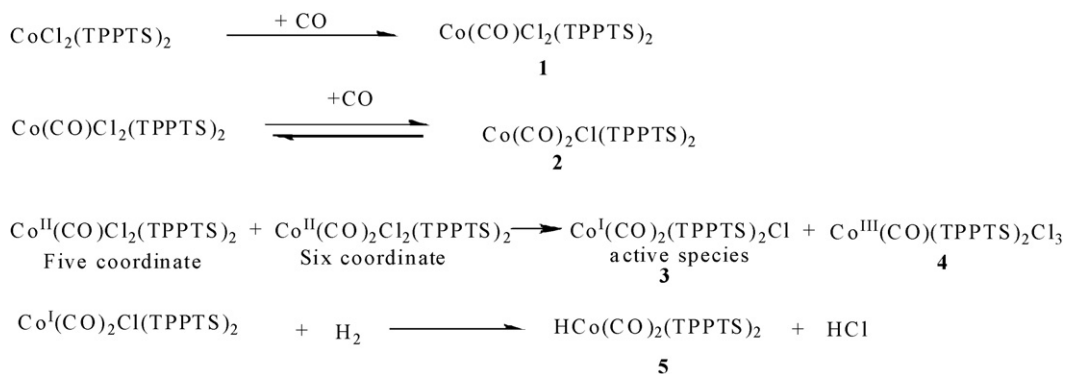
TPPTS/cat (mmol)	Conversion (%)	Selectivity (%)			<i>n/i</i> ratio	Org/aqueous phase separation time (min)
		1-octene	<i>n</i> -octane	2- and 3-octene		
0	98	1	4	95	2.3	60
10	97	1	3	96	2.4	15
16	97	2	4	94	2.6	05

Reaction conditions: substrate/cat = 700; solvent (water) = 25 ml; [CTAB] = 5.5 mmol/l; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.

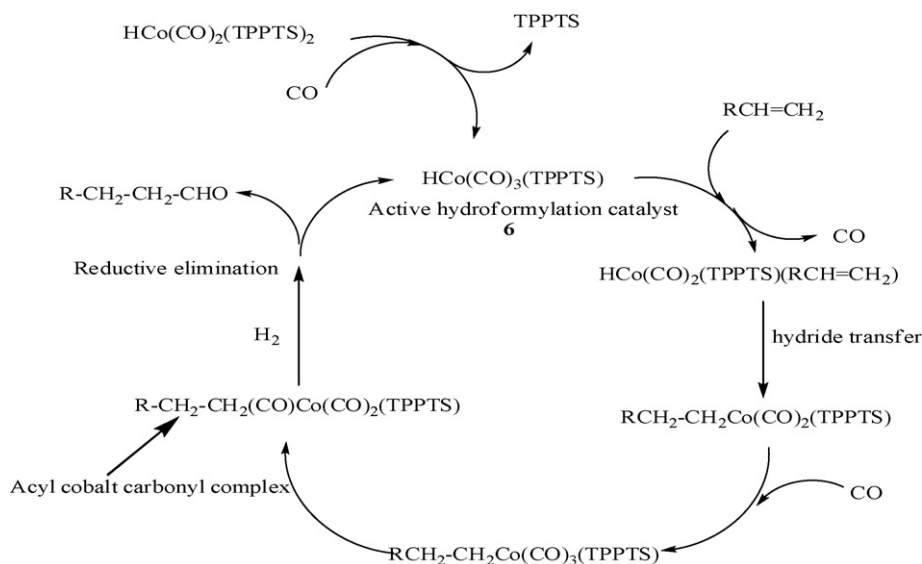
Table 7
Catalyst recycle tests: $\text{CoCl}_2(\text{TPPTS})_2$ catalyzed hydroformylation of 1-octene and 1-decene

Run	Conversion (%)	Selectivity (%)			<i>n/i</i> ratio
		<i>n</i> -octane	Isomer	Aldehyde	
1-octene					
1	97	2	4	94	2.6
2	97	1	5	94	2.6
3	97	2	5	93	2.6
4	96	1	6	93	2.5
Run	Conversion (%)	Selectivity			<i>n/i</i> ratio
		<i>n</i> -decane	Isomer	Aldehyde	
1-decene					
1	95	2	8	90	2.3
2	94	2	11	87	2.3
3	95	1	12	87	2.3
4	95	2	11	87	2.3

Reaction conditions: substrate/cat = 700; TPPTS/cat = 16; [CTAB] = 5.5 mmol/l; solvent (water) = 25 ml; temperature = 100 °C; pressure = 8 MPa; reaction time = 5 h.



Scheme 1. Interaction of $\text{CoCl}_2(\text{TPPTS})_2$ with syngas.



Scheme 2. Mechanism of hydroformylation reaction.

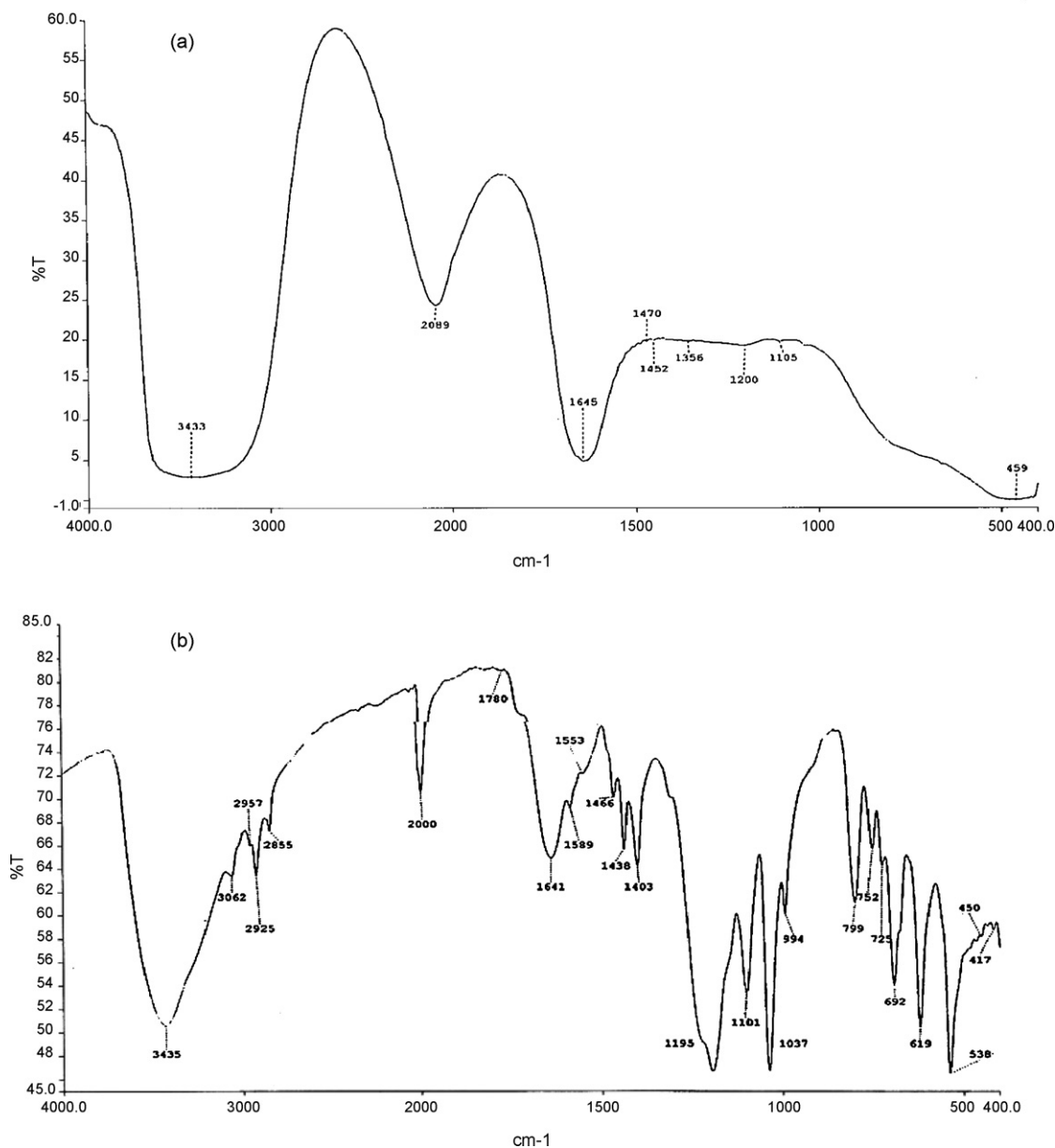


Fig. 2. (a) The IR spectra of the aqueous reaction mixture as such after the hydroformylation of 1-octene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$; (b) the IR spectra of the used catalyst after drying the aqueous reaction mixture of the hydroformylation of 1-octene catalyzed by $\text{CoCl}_2(\text{TPPTS})_2$.

of similar five and six coordinated cobalt carbonyl species having triphenylphosphine have been reported by Bressan et al. [44] by the interaction of $\text{CoCl}_2(\text{PPh}_3)_2$ with CO. The six coordinated complex, $\text{Co}(\text{CO})_2(\text{TPPTS})_2\text{Cl}_2$ can react with five coordinated cobalt intermediate by redox bridging mechanism to give $\text{Co}^{\text{I}}(\text{CO})_2(\text{TPPTS})_2\text{Cl}$ (3) species and unstable $\text{Co}^{\text{III}}(\text{CO})(\text{TPPTS})_2\text{Cl}_3$ (4) complex [44]. Further reaction of 3 with H_2 gives $\text{HCo}(\text{CO})_2(\text{TPPTS})_2$ (5). Finally $\text{HCo}(\text{CO})_2(\text{TPPTS})_2$ reacts with carbon monoxide, and with the dissociation of TPPTS, gives active catalytic species $\text{HCo}(\text{CO})_3(\text{TPPTS})$ (6) which coordinates with olefin which is followed by hydride transfer to alkenes to give four coordinated cobalt carbonyl species. Further addition of CO gives five coordinated alkyl cobalt carbonyl species. The CO insertions

give four coordinated acylcobalt carbonyl complex followed by reductive elimination to give corresponding aldehyde and active hydrido cobalt carbonyl species. The IR spectra of the aqueous reaction mixture gave a broad and strong peak at 2089 cm^{-1} (Fig. 2a) whereas the reported IR peak for $\text{HCo}(\text{CO})_3(\text{Bu}_3\text{P})$ is at 2049 cm^{-1} [40]. The aqueous solution on drying gave IR peak at 2000 cm^{-1} (Fig. 2b), that could be due to $\text{Co}(\text{CO})(\text{TPPTS})_2\text{Cl}_2$ (1) [44] formed initially.

4. Conclusions

$\text{CoCl}_2(\text{TPPTS})_2$ was found to be effective catalyst for hydroformylation of 1-octene and 1-decene at $100\text{ }^\circ\text{C}$ temperature and 8 MPa pressure. The addition of CTAB to biphasic hydroformy-

lation catalytic reaction improves the catalyst activity while retaining aldehyde selectivity. The addition of TPPTS brings down the leaching of the cobalt from aqueous phase to organic phase and facilitates the separation of organic–aqueous phase.

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