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Biphasic hydroformylation of 1-octene catalyzed by cobalt complex of trisulfonated tris(biphenyl)phosphine

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ABSTRACT

The aqueous biphasic hydroformylation of 1-octene catalyzed by cobalt complex of the water-soluble ligand trisulfonated tris(biphenyl)phosphine (BiphTS) was investigated in the absence and presence of various mass transfer promoters (co-solvents, surfactants, cyclodextrins and activated carbon). In the presence of cetyltrimethylammonium bromide, methylated β-cyclodextrin or activated carbon, the Co/BiphTS system allowed the hydroformylation of 1-octene with high conversion (92–95%) and aldehydes selectivity (85–90%). Moreover, the catalytic system could be easily reused in the presence of activated carbon as a mass-transfer promoter. In all cases, the conversion and the aldehydes selectivity were found to depend strongly on the ligand/cobalt ratio.

1. Introduction

Hydroformylation of olefins is an important industrial process to produce aldehydes catalyzed by cobalt or rhodium based metal complex [1–5]. The separation of the catalyst being dissolved in the reaction medium becomes difficult with increasing molecular weight of olefin. Among the different approaches to separate the catalyst from the products [6], aqueous biphasic catalysis is of great interest as it provides an easy separation of products and catalyst by using water a benign solvent. Moreover, this strategy has proven its commercial feasibility in the hydroformylation of propene developed by Ruhr Chemie–Rhone Poulenc [7–9]. In this approach, the catalyst is effectively anchored in the aqueous phase by means of the water soluble ligands. Among the various water-soluble ligands, trisodium salt of tris(*m*-sulfophenyl) phosphine $P(3\text{-}C_6H_4SO_3Na)_3$ (TPPTS) is one the most commonly used ligand due to its excellent coordinated ability and solubility in water [10–12]. The synthesis of TPPTS is difficult because of the use of fuming sulfuric acid and long reaction time (usually several days) which led to the formation of phosphine oxide as impurity. The problem could be avoided by introducing activating groups like methyl, methoxy on the phenyl rings [13,14]. However, the catalytic activities and chemioselectivities obtained with these ligands are different of those observed with TPPTS [15].

We have recently reported that the sodium salt of trisulfonated tris(biphenyl)phosphine (BiphTS) could advantageously used instead of TPPTS [16]. BiphTS exhibits high solubility in water (~1.0 kg L^{-1}) and is much more accessible from a synthetic point of view than TPPTS. Indeed, the sulfonation conditions for BiphTS are much softer as concentrated H_2SO_4 (98%) is used instead of oleum 60%. Furthermore, this phosphine appeared also to be a genuine water-soluble analogue of the organic PPh_3 as it displayed similar cone angle and basicity to PPh_3. Other important difference between BiphTS and TPPTS is that the TPPTS is susceptible to oxidation. The yield of TPPTS is lower in the tune of about 15–20% due to the formation of its oxide during its synthesis while BiphTS is not easily oxidized [16].

Herein, we report the application of BiphTS as a ligand in cobalt catalyzed hydroformylation of 1-octene and describe influence of various mass transfer additives on the conversion and selectivity. The development of an aqueous biphasic phosphine modified cobalt hydroformylation technology is a great interest as the cobalt catalysts are less expensive than rhodium catalysts and are able to hydroformylate internal olefins selectively to linear aldehydes [17–19].

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2. Experimental

2.1. General remarks

The sodium salt of trisulfonated tris(biphenyl)phosphine (BiphTS) was prepared according to a procedure previously reported [16]. The purity of BiphTS was carefully controlled. In particular, ^{1}H and ^{31}P NMR analysis indicated that less than 1% of its oxide was present. The syngas, CO/H_2 (1:1) with purity of 99.9% used was from Hydro Gas India Pvt. Ltd., India. 1-octene, CTAB, β-cyclodextrin and RAME-β-CD were purchased from M/s. Aldrich Chemicals, USA. The $CoCl_2{\cdot}6H_2O$ used in the reaction was purchased from Merck, India. Distilled and deionised water was used in all experiments.

Water-soluble cobalt complex $CoCl_2(BiphTS)_2$ was synthesized following the procedure reported by Cotton et al. for the synthesis of $CoCl_2(PPh_3)_2$ [20]. The commercial activated carbon Nuchar WV-B denoted as AC-WV used as catalyst support was supplied by MeadWestvaco Corporation, Covington, USA. It was produced from wood and activated by a phosphorus acid. AC-WV has a large surface area (1690 m^2/g), pore volume (1.32 cm^3/g), and average pore size (3.1 nm).

2.2. Instrumentation

The hydroformylation reactions were performed in 100 mL stainless steel autoclave (Autoclave Engineers, EZE-Seal Reactor, USA). ^{31}P NMR spectra of ligand and metal complex were measured in D_2O using 85% H_3PO_4 as an internal reference on Bruker Avance 500 MHz FT-NMR. IR spectra were recorded using nujol mull and KBr pellet on PerkinElmer spectrum GX FT-IR system in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The UV–vis spectra were recorded on UV–vis spectrophotometer (Shimadzu UV-3101PC) at room temperature in the wavelength range of 200–800 nm. Elemental analyses were done on PerkinElmer, 2400 C, H, N, S and O analyzer. X-ray photoelectron spectroscopy (XPS) was performed using a Multilab-2000 (Thermo-scientific UK) spectrometer. MALDI-TOF mass spectra were acquired using Ultraflex TOF/TOF, Bruker Daltonics Germany which is equipped with a nitrogen laser ($\lambda = 337$ nm). Products were analyzed on a Shimadzu GC-17A gas chromatograph (GC) using flame ionization detector (FID) having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter). Column temperature was initially kept at 50 °C for 5 min and then raised to 200 °C at 10 °C/min. n-decane was used as internal standard and the GC was also calibrated using known amount of corresponding aldehydes.

2.3. General procedure for hydroformylation

In the case of surfactant and cyclodextrins, a typical hydroformylation experiment was conducted as follow: a required amount of cobalt catalyst, ligand, surfactant/cyclodextrins, substrate (1-octene) and solvent were charged into the reactor. The reactor was flushed three times with nitrogen followed by flushing with syngas twice at room temperature. Then, the reactor was brought to desire reaction temperature and pressurized with syngas. The reaction was initiated by stirring (1000 rpm). After preset reaction time, the stirring was stopped, reactor was cooled down to room temperature, depressurized, flushed with N_2 and opened to collect final sample for a GC analysis.

In the case of activated carbon AC-WV, a typical hydroformylation experiment was conducted as follow: a required amount of cobalt catalyst, ligand, AC-WV and water were charged into the reactor and the resulting catalytic suspension was stirred at room temperature under 5.0 MPa syngas pressure for 12 h. Then, 1-octene (17.82 mmol), decane (200 mg; used as an internal standard) were dissolved in n-hexane (12 g) and transferred into the catalytic suspension. Then, hydroformylation reaction was performed in autoclave reactor as per method describe above. After reaction, the liquid and the solid were separated by filtration and finally, organic phase was separated for GC analysis. For reusability of catalyst, after filtration and decantation, the recovered aqueous phase and recovered AC-WV were reloaded in autoclave with fresh 1-octene, decane (internal standard), n-hexane (solvent) as described above.

2.4. Determination of cobalt contents in organic layer

To determine cobalt content in organic layer at the end of the hydroformylation reaction, the organic layer was separated from the aqueous layer and volatile compounds were removed under reduce pressure. The organic layer was treated by aqua regia under refluxing condition for overnight and then evaporated to dryness. The distilled water was added into the remaining mass and filtered. The cobalt contents in the aqueous solution were determined by ICP-OES.

3. Results and discussion

3.1. Characterization

The BiphTS ligand and $CoCl_2(BiphTS)_2$ complex were characterized by physicochemical techniques. The results of elemental analyses were consistent with those calculated for $CoCl_2(BiphTS)_2$ complex, [Calc. (Found) %: C, 25.07 (25.65); H, 1.39 (1.57)]. ^{31}P NMR spectrum of $CoCl_2(BiphTS)_2$ complex gave a broad singlet at 53.5 ppm (may be due to the paramagnetic nature of the complex or equilibrium between Co species and free phosphine in solution) indicating the equivalence of two phosphorous atoms of BiphTS. IR spectrum of $CoCl_2(BiphTS)_2$ complex gave bands at 1191 cm^{-1} for νSO_3^-, 1125 cm^{-1} for νSO, 638 cm^{-1} for $\nu' SO$, 1481, 1385, 815 and 715 cm^{-1} for νph. The coordination of ligand and nature of coordinated BiphTS ligand in $CoCl_2(BiphTS)_2$ were also probed by UV–vis spectroscopy comparing the UV–vis spectrum of a free ligand with that of $CoCl_2(BiphTS)_2$ complex. The UV–vis spectrums of $CoCl_2{\cdot}6H_2O$, BiphTS ligand and $CoCl_2(BiphTS)_2$ complex in H_2O are presented in Fig. 1.

A UV–vis spectrum of a free BiphTS ligand exhibited one high intense absorption band at 271 nm whereas no band appeared at higher wavelengths. This is reasonable accordance with literature of PPh_3 (at 260 nm) [21]. A UV–vis spectrum of $CoCl_2{\cdot}6H_2O$ displayed two weak absorption bands at 512 and 545 nm. The cobalt complex, $CoCl_2(BiphTS)_2$ revealed a intense broad absorption band at 281 nm and other two weak bands at higher wavelength of 503 and 551 nm (Fig. 1). The similar three absorption bands were observed for $CoCl_2(PPh_3)_2$ complex [20,22]. The shift and broadening of absorption band at 281 nm in the UV–vis spectrum of $CoCl_2(BiphTS)_2$ indicates a dynamic ligand exchange in the complex and characteristic of pseudo-tetrahedral Co(II) complex [20,22].

Based on the literature data [23–25] and experimental study, a reaction scheme is proposed for the formation of active catalytic species $HCo^{I}(CO)_3(BiphTS)$ from $Co^{II}Cl_2(BiphTS)_2$ (Scheme 1). The carbon monoxide reacts with cobalt complex, $CoCl_2(BiphTS)_2$ to give a five coordinated complex, $Co(CO)(BiphTS)_2Cl_2$ (**1**) and then six coordinated cobalt carbonyl complexes $Co(CO)_2(BiphTS)_2Cl_2$ (**2**), which are in equilibrium. The six coordinated complex, $Co(CO)_2(BiphTS)_2Cl_2$ (**2**) can react with five coordinated cobalt intermediate (**1**) by redox bridging mechanism to give $Co^{I}(CO)_2(BiphTS)_2Cl$ (**3**) species and unstable $Co^{III}(CO)(BiphTS)_2Cl_3$ (**4**) complex [25]. The formation of similar five, six coordinated

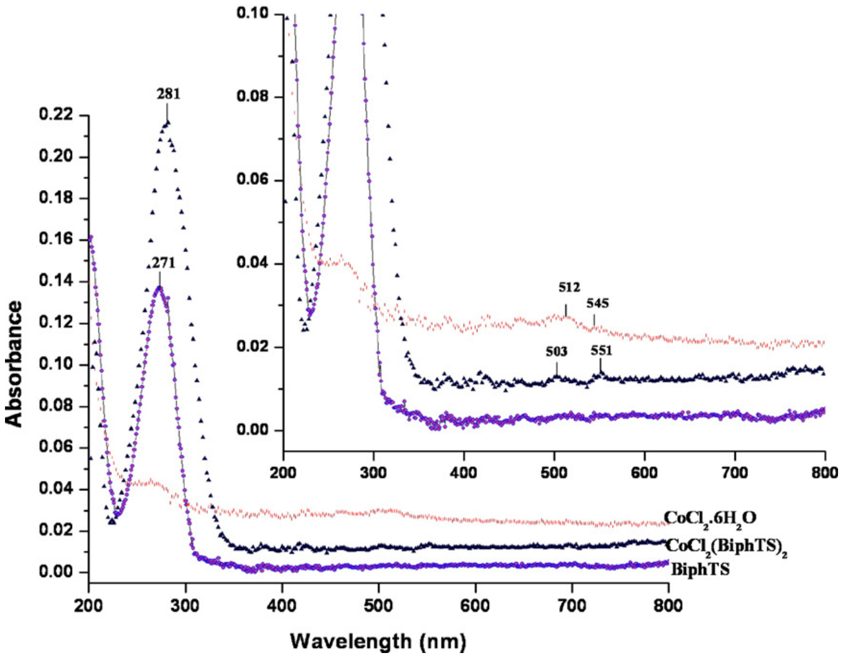
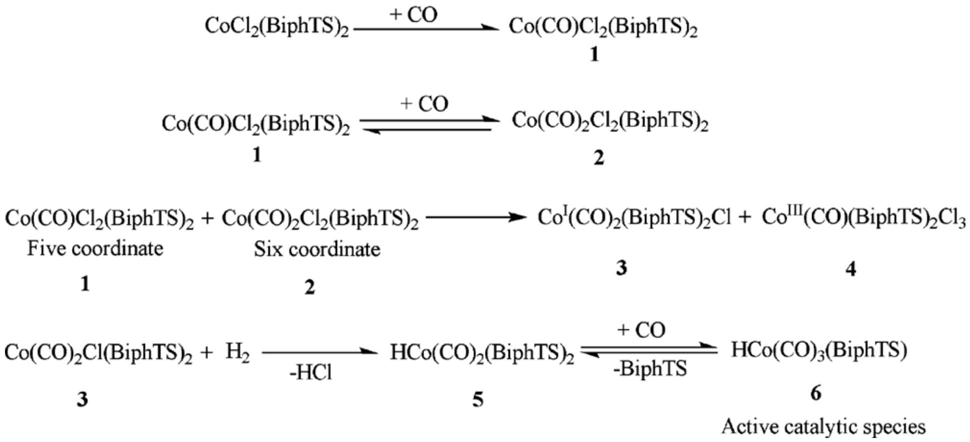


Fig. 1. UV–vis spectrums of $CoCl_2{\cdot}6H_2O$, $CoCl_2(BiphTS)_2$ and BiphTS.

cobalt carbonyl species and Co(I) carbonyl complex with PPh_3 have been reported by Bressan et al. [25] by the interaction of $CoCl_2(PPh_3)_2$ with CO. In order to ascertain the formation of such cobalt carbonyl complexes in the case of $CoCl_2(BiphTS)_2$, one experiment was conducted under CO (4 MPa) at 100 °C with $CoCl_2(BiphTS)_2$ in water. After 3 h, the resulting solution was evaporated *in vacuo* to give solid. The infrared spectra of solid so obtained displayed a band at 1920 cm^{-1} and a shoulder in the region of 2010–2020 cm^{-1} (Fig. 2b) which confirms the formation of $Co(CO)_2(BiphTS)_2Cl_2$ (**2**) and/or $Co^I(CO)_2(BiphTS)_2Cl$ (**3**).

Indeed, these values are in reasonable accordance with literature values of $Co(CO)_2(PPh_3)_2Cl$ at 1919 and 1984 cm^{-1}[26]. The reaction of (**3**) with H_2 gives $HCo(CO)_2(BiphTS)_2$ (**5**). Finally $HCo(CO)_2(BiphTS)_2$ reacts with CO and with the dissociation of ligand BiphTS, gives active catalytic species $HCo(CO)_3(BiphTS)$ (**6**). In order to confirm the formation of such active hydrido cobalt carbonyl species $HCo(CO)_3(BiphTS)$ by interaction of syngas with $CoCl_2(BiphTS)_2$, another experiment was carried out with $CoCl_2(BiphTS)_2$ in water under syngas (8 MPa) at 100 °C. After 6 h, the IR spectra of the resulting aqueous solution gave a broad and strong peak at 2090 cm^{-1} (Fig. 2c) analogous with the reported IR peak for $HCo(CO)_3(TPPTS)$ at 2089 cm^{-1} [3]. The aqueous solution on evaporated *in vacuo* gave IR peak at 2000 cm^{-1} and 1951 cm^{-1} (Fig. 2d), that could be due to the mixture of $Co(CO)_3(BiphTS)_2$ or $Co_2(CO)_6(BiphTS)_2$ as hydrido cobalt carbonyl species is stable only syngas environment and attempts to isolate yielded mixture of cobalt carbonyl complexes [27]. The MALDI-TOF–MS analysis of resulting compound obtained by evaporating the aqueous phase after reaction of $CoCl_2(BiphTS)_2$ with syngas also confirmed the formation of such cobalt carbonyl complexes (see Supporting information).

In order to confirm the possible oxidation states of Co ion the XPS analysis of Co/BiphTS complexes was carried out. The high resolution Co 2p XPS spectra of $CoCl_2(BiphTS)_2$ and resulting compound, $Co^I(CO)_x(BiphTS)_y$ abbreviated as CoCOBT obtained by evaporating the aqueous phase after reaction of $CoCl_2(BiphTS)_2$ with syngas (8 MPa,100 °C) are presented in Fig. 3. The Co 2p region of $CoCl_2(BiphTS)_2$ exhibited four peaks; two main peaks due to Co 2p(3/2), Co 2p(1/2) and the shake up resonance transitions (satellites) of these two peaks above the 2p(3/2) transition (Fig. 3a). The Co 2p(3/2) and Co 2p(1/2) binding energies obtained as 782.6



Scheme 1. Interaction of $CoCl_2(BiphTS)_2$ with syngas.

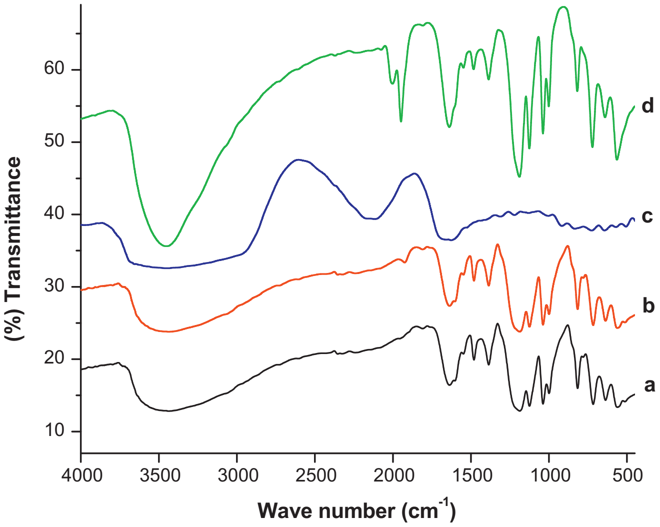


Fig. 2. FT-IR spectra of $CoCl_2(BiphTS)_2$ and cobalt carbonyl intermediate species. (a) IR spectrum of $CoCl_2(BiphTS)_2$; (b) IR spectrum of the compound after reaction of $CoCl_2(BiphTS)_2$ with CO; (c) IR spectrum of the aqueous phase after reaction of $CoCl_2(BiphTS)_2$ with syngas; (d) IR spectrum of the resulting compound obtained by evaporating the aqueous phase after reaction of $CoCl_2(BiphTS)_2$ with syngas.

and 798.6 eV respectively. These binding energies are very close to those reported for Co^{+2} ions [28]. Comparison of XPS data of Co 2p in $CoCl_2(BiphTS)_2$ with that of CoCOBT indicate that the binding energies (BE) of Co 2p(1/2) and Co 2p(3/2) in CoCOBT complex shifted from 798.6 to 797.3 eV and 782.6 to 781.4 eV respectively. The known complex of Co(I) $[Co(CO)_3(PPh_3)_2]^+$ exhibits the Co 2p(3/2) peak at 781.9 eV [28]. Similarly the complex CoCOBT displayed Co 2p(3/2) peak at 781.4 eV (Fig. 3b) confirming that the cobalt carbonyl complex CoCOBT is also a Co(I) compound. In addition, the presence and absence of the satellites peaks in XPS analysis clearly distinguish between Co(II) and Co(I) species, because the main Co(II) depict satellites (shake-up peaks) whereas the Co(I) do not [28]. As shown in Fig. 3a, in $CoCl_2(BiphTS)_2$, the Co 2p(3/2) peak is accompanied by the intense shake-up signals on the high binding-energy characteristic of Co(II) while in CoCOBT only a weak shake-up single supplement with 2p(3/2) peak was observed.

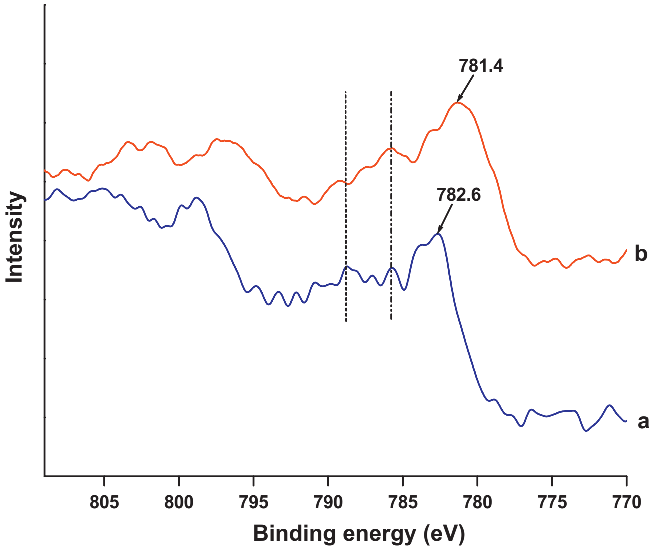


Fig. 3. The high resolution Co 2p XPS spectra of $CoCl_2(BiphTS)_2$ (a) and resulting compound (b) obtained by evaporating the aqueous phase after reaction of $CoCl_2(BiphTS)_2$ with syngas.

The catalytic performance of water-soluble ligand, BiphTS was then evaluated in cobalt catalyzed hydroformylation of 1-octene in the absence and presence of various mass transfer promoters. Reaction products were nonanal (linear aldehyde) and 2-methyl octanal (branched aldehyde) represented as linear to branched aldehyde ratio (l/b). Side products were internal octenes (2-octene, 3-octene) and octane resulted from 1-octene isomerization and hydrogenation. As the selectivity of products in hydroformylation reaction mainly depends on the parameters such as temperature, syngas pressure, ligand/Co ratio, the hydroformylation experiments were carried out by varying these parameters.

3.2. Co/BiphTS catalyzed hydroformylation of 1-octene in the absence of mass transfer promoters

In the absence of any mass transfer promoters, the hydroformylation of 1-octene catalyzed by the Co/BiphTS system showed low activity due to the poor solubility of 1-octene in water. Effect of temperature and syngas pressure on conversion and selectivity was studied for determining the optimum condition. The results are summarized in Table 1.

Temperature was varied from 90 to 130 °C at constant syngas pressure (8.0 MPa). With an increase in temperature, the conversion and isomerization of 1-octene increased (Table 1). However, aldehydes chemoselectivity and l/b aldehyde ratio were found to decrease with an increase in temperature. The decrease in aldehydes selectivity at higher temperature is mainly due to the increase in the isomerization products. Indeed, it is well known that internal alkenes are more difficult to hydroformylate than terminal alkenes [17]. The best agreement between conversion and aldehyde selectivity was achieved at 120 °C. The hydroformylation of 1-octene catalyzed by Co/BiphTS system was then studied at 120 °C under different syngas pressure (Table 1). The total syngas pressure was found to affect the conversion and aldehyde selectivity. The results indicated that the hydroformylation of 1-octene proceed slowly at low syngas pressure. The conversion and aldehyde selectivity were increased with an increase in the syngas pressure whereas the isomerization decreased gradually with increase in the syngas pressure.

As TPPTS is a benchmark ligand in aqueous organometallic catalysis, the catalytic activity of the Co/BiphTS system was compared with the catalytic activity of Co/TPPTS system. The Co/BiphTS system was slightly less active and selective than the Co/TPPTS system (Table 1, compare entry 8 with 2). This can be explained by the fact that BiphTS is comparatively more basic than TPPTS. Indeed, BiphTS can bind more strongly to cobalt than TPPTS leading to a lower concentration of catalytically active species $HCo(CO)_3L$.

The effect of BiphTS/Catalyst ratio on the conversion and selectivity of 1-octene hydroformylation was studied at 120 °C and 8.0 MPa by varying ligand/Catalyst ratio (Table 2). An increase in the BiphTS/Catalyst ratio had noticeable effect on the conversion and the selectivity. The conversion of 1-octene decreased from 36 to 12%. However, aldehyde selectivity and l/b aldehyde ratio were increased from 45 to 48% and 2.3 to 2.5, respectively. The leaching of cobalt from aqueous phase to the organic phase decreased from 1.6 to 0.05 ppm with an increase in BiphTS concentration (Table 2). These results can be rationalized by considering the equilibrium between the species $HCo(CO)_2L_2$ (**5**) and the catalytic active species $HCo(CO)_3L$ (**6**). As BiphTS is comparatively more basic than TPPTS, the equilibrium between $HCo(CO)_2L_2$ and $HCo(CO)_3L$ is likely shifted towards the less active $HCo(CO)_2L_2$ species in presence of excess ligand. It is also notice that effect of BiphTS/Co ratio on the conversion and selectivity is much more pronounced than in the case of the TPPTS (Table 2) [3]. These results also confirm that the BiphTS ligand coordinates more strongly to Co catalyst than TPPTS. Although the reaction can also occur in the organic phase

Table 1
Effect of temperature and pressure on hydroformylation of 1-octene catalyzed by $CoCl_2(BiphTS)_2$ in aqueous medium.[a]

Entry	Temp. (°C)	Press. (MPa)	Conv. (%)	S_{alkane} (%)	S_{isomer} (%)	$S_{aldehyde}$ (%)	l/b
1	90	8	12	–	31	69	2.6
2	100	8	23	2	38	60	2.5
3	110	8	31	6	45	49	2.3
4	120	8	36	8	47	45	2.3
5	130	8	45	12	58	30	2.1
6	120	9	38	10	42	48	2.2
7	120	7	34	20	53	27	2.2
8[b]	100	8	29	9	26	65	2.8

[a] Reaction conditions: 1-octene = 17.82 mmol, $[CoCl_2(BiphTS)_2]$ = 0.48 mM, decane = 200 mg, solvent (water) = 25 mL, reaction time = 5 h.
[b] $CoCl_2(TPPTS)_2$ was used instead of $CoCl_2(BiphTS)_2$.

Table 2
Effect of BiphTS concentration on hydroformylation of 1-octene catalyzed by $CoCl_2(BiphTS)_2$ catalyst.[a]

Entry	Add. BiphTS/Cat.	Conv. (%)	S_{alkane} (%)	S_{isomer} (%)	$S_{aldehyde}$ (%)	l/b	Co leaching (ppm)
1	–	36	8	47	45	2.3	1.6
2	2:1	27	7	47	46	2.3	1.1
3	4:1	20	8	46	46	2.4	0.6
4	6:1	12	7	45	48	2.5	0.05

[a] Reaction conditions: 1-octene = 17.82 mmol, $[CoCl_2(BiphTS)_2]$ = 0.48 mM, Temp. = 120 °C, Press. = 8 MPa, decane = 200 mg, solvent (water) = 25 mL, reaction time = 5 h.

due to the presence of water insoluble hydrido species $HCo(CO)_x$ (x: 3,4) under CO/H_2 pressure and high temperature, the ICP-OES analyses demonstrate that the catalytic system is immobilized into the aqueous phase when the reaction mixture is cooled and depressurized to ambient conditions. Indeed, the amount of cobalt in the organic phase at the end of the reaction was very low and decreased notably when the phosphine/cobalt ratio increased (Table 2).

3.3. Co/BiphTS catalyzed 1-octene hydroformylation in the presence of mass transfer promoters

In order to improve the solubility of 1-octene in aqueous media, co-solvents, surfactants and modified cyclodextrins have been used. In the presence of co-solvents (methanol and ethanol), 1-octene conversion was increased up to 58 and 56% with aldehyde selectivity to 54 and 55% in methanol and ethanol respectively (Table 3, entries 1 and 2). In the case of native β-cyclodextrin, the conversion was increased up to 66% with 50% aldehyde chemoselectivity (Table 3, entry 6). The cetyltrimethylammonium bromide (CTAB) and randomly methylated β-cyclodextrin (RAME-β-CD) greatly enhanced the conversion and the aldehyde selectivity. Thus, high conversion (95%) with 85–86% aldehyde selectivity was obtained in the case of CTAB and RAME-β-CD. However, the l/b aldehyde ratio dropped from 2.3 to 1.3 while using RAME-β-CD. The beneficial effect of such additives on the mass transfer is well documented in the literature and has been attributed to the formation of micelles and inclusion complexes between the substrate and the cyclodextrin [29–34]. For example, the CTAB form cationic micelle which augment the anionic catalytic species on the surface of micelles through the static attraction and dissolved the olefin in the inner micelle to increase the coordination of olefin with catalytic species. The TPPTS and BiphTS both have anionic SO_3^- group (Fig. 4). The addition of mass transfer additives increased the conversion and aldehyde selectivity in the case of Co/BiphTS too. This clearly evident that role of mass-transfer agents is same in the both TPPTS and BiphTS ligands. As expected, a decrease in the concentration of CTAB and RAME β-CD led to lower activities. In the case of RAME-β-CD, the formation of an emulsion at the end of reaction was not observed and separation of the aqueous and organic phase was rapid.

The effect of BiphTS concentration in presence of CTAB and RAME-β-CD was also investigated. The BiphTS/Catalyst ratio was varied from 2 to 6 at constant 5.5 mM CTAB (Table 4, entries 2–4) and 10 mM RAME β-CD concentration (Table 5, entries 2–4). When BiphTS concentration increased, the 1-octene conversion and aldehyde selectivity were remarkably decreased in both cases. In the case of CTAB, the conversion of 1-octene and the aldehydes selectivity decreased from 95 to 60% and from 86 to 68%, respectively. While in the case of RAME-β-CD, the 1-octene conversion decreased from 95 to 51% with the decreasing in the aldehyde selectivity from 85 to 65%. On the other hand, it was observed that separation time of aqueous and organic phases after end of the reaction decreased with an increasing in BiphTS concentration in the case of CTAB. Compared to Co/TPPTS system, the addition of excess BiphTS ligand decreases conspicuously the conversion and aldehyde selectivity [3,19]. These results are in agreement with those obtained without mass transfer additives and confirm that the BiphTS ligand coordinates more strongly to Co species than TPPTS. In order to increase the 1-octene conversion and aldehyde selectivity, we also combined co-solvent with CTAB and increased syngas pressure (9.0 MPa). The conversion was increased (60–75%) with aldehyde chemoselectivity increased from 68 to 78% (Table 4, entry 5). Whereas the concentration of RAME-β-CD increased from 10 mmol to 40 mmol/L, the conversion was increased (51–62%) with aldehyde chemoselectivity increased from 65 to 70% (Table 5, entry 5).

Recently, the possibility of using an activated carbon as a mass transfer additive in aqueous organometallic catalysis has been

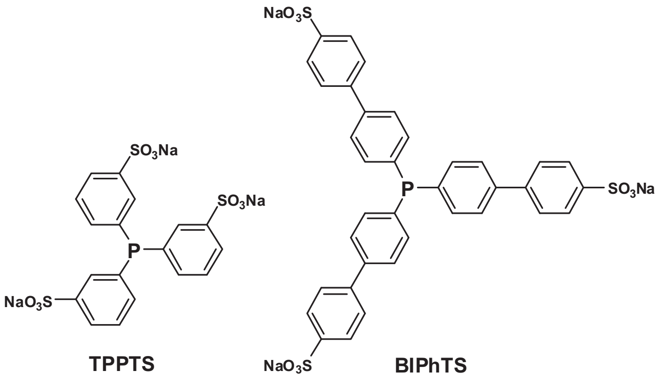


Fig. 4. Structure of trisodium salt of tris(m-sulfophenyl) phosphine (TPPTS) and trisodium salt of trisulfonated tris(biphenyl)phosphine (BiphTS).

Table 3
Effect of co-solvents, surfactants and cyclodextrins on hydroformylation of 1-octene catalyzed by $CoCl_2(BiphTS)_2$.[a]

Entry	Co-solvent	Mass transfer additive (mmol/L)	Conv. (%)	S_{alkane} (%)	S_{isomer} (%)	$S_{aldehyde}$ (%)	l/b
1	Methanol	–	58	6	40	54	2.1
2	Ethanol	–	56	6	39	55	2.1
3	–	CTAB (2.5)	79	5	12	83	2.2
4	–	CTAB (4.5)	85	6	11	83	2.1
5	–	CTAB (5.5)	95	4	10	86	2.1
6	–	β-CD (15)	66	7	43	50	1.5
7	–	RAME-β-CD (5)	90	5	14	81	1.3
8	–	RAME-β-CD (10)	95	5	10	85	1.3

[a] Reaction conditions: 1-octene = 17.82 mmol, $[CoCl_2(BiphTS)_2]$ = 0.48 mM, Temp. = 120 °C, Syngas pressure = 8.0 MPa, decane = 200 mg, co-solvent = 5 mL, solvent (water) = 20 mL, reaction time = 5 h.

Table 4
Effect of BiphTS concentration in presence of CTAB on hydroformylation of 1-octene catalyzed by $CoCl_2(BiphTS)_2$ catalyst.[a]

Entry	Add. BiphTS/Cat.	Time (h)	Conv. (%)	S_{alkane} (%)	S_{isomer} (%)	$S_{aldehyde}$ (%)	l/b	Org/aqua. Phase separation time (min)
1	–	5	95	4	10	86	2.1	60
2	2:1	5	75	6	33	61	2.1	15
3	4:1	9	65	5	31	64	2.2	05
4	6:1	9	60	5	27	68	2.3	05
5[b]	6:1	9	75	5	17	78	2.2	05

[a] Reaction conditions: 1-octene = 17.82 mmol, $[CoCl_2(BiphTS)_2]$ = 0.48 mM, Temp. = 120 °C, Syngas pressure = 8.0 MPa, CTAB = 5.5 mmol/L, decane = 200 mg, solvent (water) = 25 mL.

[b] Co-solvent (methanol) = 5 mL, [CTAB] = 6.0 mmol/L, Press. = 9.0 MPa.

Table 5
Effect of BiphTS concentration in presence of RAME-β-CD on hydroformylation of 1-octene catalyzed by $CoCl_2(BiphTS)_2$ catalyst.[a]

Entry	Add. BiphTS/Cat.	Time (h)	Conv. (%)	S_{alkane} (%)	S_{isomer} (%)	$S_{aldehyde}$ (%)	l/b
1	–	5	95	5	10	85	1.3
2	2:1	5	71	6	46	58	1.3
3	4:1	10	60	5	34	61	1.4
4	6:1	10	51	5	30	65	1.5
5[b]	6:1	10	62	5	25	70	1.5

[a] Reaction conditions: 1-octene = 17.82 mmol, $[CoCl_2(BiphTS)_2]$ = 0.48 mM, Temp. = 120 °C, Press. = 8 MPa, [RAME-β-CD] = 10 mmol/L, decane = 200 mg, solvent (water) = 25 mL.

[b] [RAME-β-CD] = 40 mmol/L.

Table 6
Hydroformylation of 1-octene catalyzed by $CoCl_2(BiphTS)_2$ in presence of AC-WV.[a]

Entry	Add. BiphTS/Cat	Conv. (%)	S_{alkane} (%)	S_{isomer} (%)	$S_{aldehyde}$ (%)	l/b
1[b]	–	53	2	23	75	1.5
2[b,c]	–	56	2	22	76	1.5
3	–	82	7	30	63	1.3
4	4	51	2	30	68	1.6
5[d]	4	85	2	32	75	1.5
6[d]	2	92	–	10	90	1.3
7[e]	2	96	–	08	93	1.3
1st recycle[d]	2	92	–	12	88	1.3
2nd recycle[d]	2	92	–	14	86	1.2
3rd recycle[d]	2	88	–	15	85	1.2

[a] Reaction conditions: 1-octene = 17.82 mmol, $[CoCl_2(BiphTS)_2]$ = 0.6 mM, AC-WV = 50 mg, Temp. = 120 °C, Press. = 9 MPa, decane = 200 mg, water = 20 mL, n-hexane = 12 g, reaction time = 6 h.

[b] Temp. = 90 °C.

[c] AC-WV = 75 mg.

[d] Reaction time = 10 h.

[e] Reaction performed with $CoCl_2(TPPTS)_2$.

reported [35]. The beneficial effect of activated carbon on the mass transfer was attributed to an increase in the interfacial area and to a confinement of catalyst and reactants in pores [35–37]. Thus, the mass transfer efficiency of activated carbon in hydroformylation of 1-octene under biphasic conditions was investigated by adding activated carbon AC-WV into catalytic solution. The results are summarized in Table 6. In order to explore precisely the influence of activated carbon AC-WV under different operating parameters such as effect of temperature, effect of BiphTS concentration, reaction time and amount of AC-WV, few control experiments were performed by varying such parameters under constant syngas pressure (9 MPa) with 50 mg of AC-WV. At 90 °C, the conversion of 1-octene is low (53%) which increased up to 82% with 63% aldehyde selectivity in 6 h at 120 °C (Table 6, entries 1 and 3). Surprisingly, the conversion of 1-octene was not greatly affected by additional (25 mg) activated carbon (Table 6, entry 2). This result indicates that 50 mg of AC-WV is sufficient to act as mass transfer promoter in present reaction system. The conversion of 1-octene noticeably decreased from 82 to 51% with an increase in the ligand/Catalyst up to 4 (Table 6, entries 3 and 4). However, the conversion and aldehyde selectivity increased significantly when reaction time increased up to 10 h (Table 6, entry 5). Interestingly, the conversion and the aldehydes selectivity reached maximum, i.e. 92 and 90%, respectively at low ligand/Catalyst ratio of 2 in 10 h (Table 6, entry 6). In order to compare the catalytic activity of the Co/BiphTS system with Co/TPPTS system, one experiment was carried out with catalyst $CoCl_2(TPPTS)_2$ under similar reaction condition (Temp. 120 °C, 9 MPa syngas pressure, ligand/Catalyst = 2 and reaction time 10 h). In this case, the conversion of 1-octene was found 96% with 93% aldehyde selectivity. From the result of $CoCl_2(TPPTS)_2$, one can conclude that the catalytic activity and selectivity of Co/BiphTS system is comparable to the Co/TPPTS system at lower ligand excess (Table 6, entry 7).

The reusability of the catalytic system was also evaluated with AC-WV at optimum reaction conditions (Temp. 120 °C, 9 MPa syngas pressure, ligand/Catalyst = 2 and reaction time 10 h). At the end of each reaction cycle, the liquid and the solid were separated by filtration and finally, organic phase was separated. Then, new organic phase containing the substrate was added into the recovered aqueous phase and along with recovered AC-WV. The catalyst recycle data showed no significant loss of activity after three consecutive runs suggesting that Co leaching into organic phase is negligible (Table 6). In order to confirm the confinement of catalyst into pores, UV–vis spectroscopy experiments were performed on the aqueous phase at the end of the reaction. A hydroformylation experiment was performed at optimum reaction conditions (120 °C, 9 MPa syngas pressure, 1-octene = 17.82 mmol, AC-WV = 50 mg, water = 20 mL, n-hexane = 12 g, reaction time = 10 h) with initial $CoCl_2(BiphTS)_2$ catalyst concentration of 0.6 mM. After reaction, the liquid and the solid were separated by filtration. Then, aqueous phase was separated from the organic phase and analyzed by UV–vis spectroscopy. The concentration of cobalt catalyst in the recovered aqueous phase was found 0.41 mM by UV–vis spectroscopy with standard solutions and dilution of recovered aqueous phase. This analysis indicated that the ~32% of catalyst was adsorbed onto the AC-WV.

4. Conclusions

The biphasic hydroformylation of 1-octene can be efficiently catalyzed by a Co/BiphTS system in the presence of various mass transfer promoters. Contrary to the TPPTS, the conversion and the aldehydes selectivity were found to be strongly dependent on the phosphine/Co ratio, indicating that the BiphTS ligand coordinate more strongly to Co species than TPPTS. The study showed also that the cobalt based catalyst is maintained in the aqueous phase at the end of the reaction in presence of low excess of ligand. Furthermore, experiments performed with an activated carbon AC-WV demonstrated that the catalytic system can be recovered and recycled without significant loss of activity. Works are currently underway to explore the behavior of the BiphTS in reactions requiring basic ligands.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.11.021.

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