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Journal of Molecular Catalysis A: Chemical 282 (2008) 99–106

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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$CoCl_2(TPPTS)_2$ catalyzed hydroformylation of 1-octene and 1-decene in the presence of surfactant and co-solvents in a biphasic medium

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Received 1 August 2007; received in revised form 31 October 2007; accepted 28 November 2007

Abstract

$CoCl_2(TPPTS)_2$ 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, $CoCl_2(TPPTS)_2$, 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.

Keywords: Biphasic catalysis; Higher olefins hydroformylation; Cobalt/TPPTS; CTAB

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: $P(m\text{-}C_6H_4SO_3Na)_3$], 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 $CoCl_2(TPPTS)_2$ [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 $CoCl_2(TPPTS)_2$ 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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doi:10.1016/j.molcata.2007.11.026

and water content was less than 10%. $CoCl_2 \cdot 6H_2O$ 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, $CoCl_2(TPPTS)_2$, was synthesized following the procedure reported by Cotton et al. [38] for the synthesis of $CoCl_2(PPh_3)_2$.

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 400–4000 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 °C for 5 min and then raised to 200 °C at 10 °C/min. Nitrogen was used as a carrier gas (1.2 ml/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, $CoCl_2(TPPTS)_2$, 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 $CoCl_2(TPPTS)_2$ 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 $CoCl_2(TPPTS)_2$ catalyzed hydroformylation of 1-octene and 1-decene performed at 60–120 °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 °C, 1-octene conversion is only 9% but selectivity towards the nonanal was 87%. At 120 °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 $CoCl_2(TPPTS)_2$ in aqueous medium

Temperature (°C)	Pressure (MPa)	Conversion (%)	Selectivity (%) for 1-octene hydroformylation			
		1-octene	*n*-octane	2- and 3-octene	Aldehyde	*n*/*i* ratio
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 (°C)	Pressure (MPa)	Conversion (%)	Selectivity (%) for 1-decene hydroformylation			
		1-decene	*n*-decane	2- and 3-decene	Aldehyde	*n*/*i* ratio
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: $[CoCl_2(TPPTS)_2] = 1.0$ mmol/l; substrate/cat = 700; decane: 0.5 ml; solvent (water) = 25 ml; reaction time = 5 h.