Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Catalysis A: General 303 (2006) 158–165

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Selective thermomorphic biphasic hydroformylation of higher olefins catalyzed by $HRhCO(PPh_3)_3/P(OPh)_3$

Jimoh Tijani, Bassam El Ali *

Chemistry Department, KFUPM, 31261 Dhahran, Saudi Arabia

Received 9 October 2005; received in revised form 21 January 2006; accepted 23 January 2006

Abstract

A thermomorphic approach to rhodium-catalyzed biphasic hydroformylation of higher olefins ($C > 6$) has been developed based on $HRhCO(PPh_3)_3/P(OPh)_3$/propylene carbonate/*n*-heptane catalytic system. The catalyst system showed excellent selectivity toward the desired linear aldehyde (*n*/*i* ratio > 8) and high catalytic activity demonstrated by the efficient recycling without significant loss of the catalyst activity. The effects of the temperature, the total pressure, the ratio of CO/H_2, the reaction time and the type of ligand have been thoroughly studied.

Keywords: Hydroformylation; Thermomorphic; Biphasic; Aldehydes; Rhodium; 1-Octene; Phosphine; Phosphite; Syngas

---

1. Introduction

The hydroformylation of olefins is one of the most important industrial processes that use transition metals as catalysts. Rhodium complexes are the most efficient catalysts for this reaction in terms of both catalytic activity and selectivity [1–3]. When the continuous distillation of the aldehydes from the reaction mixture is not feasible, different strategies have been attempted to overcome the problem of the recovery of the precious metals from the reaction mixture. Molecular catalysts immobilized on different types of supports have been widely explored; nevertheless, the low catalytic activity and the leaching out of these supported catalysts remain a challenge in this area [4].

The aqueous biphasic hydroformylation of propene to butanal by Ruhrchemie/Rhone-Poulenc process was applied successfully at industrial scale. Water soluble rhodium catalyst can be easily and completely separated from water insoluble products but this approach is less efficient for higher olefins. The reason is that the catalytic reaction occurs in aqueous phase, therefore, the application of aqueous biphasic system is limited by the solubility of the olefins in the water phase [5]. Many approaches have been proposed to overcome the mass transport limitations that are typical in the conventional aqueous biphasic system. Among these approaches, a fluorous biphasic hydroformylation was developed by Horvath and Rabai [6]. The method is based on the limited miscibility of fluorinated solvent and fluorinated ligand in hydrocarbon. However, it is questionable whether the flourous biphasic will achieve any breakthrough in the large-scale industry, because of the toxicity of perflourous solvents and ligands and risks related to ozone depletion [7,8]. The principle of thermoregulated phase transfer catalysis (TRPTC), originally developed by Bergbreiter et al. [9,10], was applied to biphasic hydroformylation by Jin et al. [7,11–15]. Other traditional biphasic catalytic systems have been considered using various polar tagged ligand such as poly(*N*-isopropylacrylamide) (PNIPAM) [16–18] and monosulfonated TRIPHOS (SULPHOS) [19].

A new concept was recently developed that involved the use of a system that itself reversibly changes from being biphasic to monophasic as a function of temperature and known as a thermomorphic biphasic or temperature-depending multicomponent solvent systems [20–24]. Thermomorphic biphasic system has been applied to hydrosilylation of 10-undecenote using propylene carbonate (PC)/cyclohexane/toluene solvent system [20,21]. The new concept was also applied to rhodium-catalyzed cooligomerization of sunflower fatty acid methyl ester (SFAME) and ethylene with PC/SFAME/dioxane solvents system and in the absence of any tagged ligand [22]. Similarly, the thermomorphic biphasic system was used

---

* Corresponding author. Tel.: +966 3 860 4491.
E-mail address: belali@kfupm.edu.sa (B. El Ali).

0926-860X/$ – see front matter
doi:10.1016/j.apcata.2006.01.044

in the isomerization-hydroformylation of *trans*-4-octene [23] and in the hydroaminomethylation of 1-octene using PC/dodecane/morpholine solvent system [24].

Recently, we have reported new catalytic systems based on rhodium (I) and (III) for the selective hydroformylation alkenes [25,26].

This paper represents our contribution that includes the use of an inexpensive, simple and conventional ligand such as $P(OPh)_3$ to develop a thermomorphic biphasic rhodium system to catalyze the hydroformylation of higher olefins (>C6). The catalyst system enhances both catalytic activity and selectivity and also improves the recycling of the reaction of the hydroformylation of alkenes and subsequently minimizing the catalyst deactivation and loss. The effects of various reaction parameters on the thermomorphic biphasic catalytic system were carefully studied.

2. Experimental

2.1. General

$HRhCO(PPh_3)_3$ and other rhodium complexes were purchased from Strem Company. Alkenes were purified by passing through neutral alumina, propylene carbonate was purchased from BDH chemicals and used without purification, and all other solvents were purchased from Sigma–Aldrich and were purified prior to usage.

^1H and ^{13}C NMR spectra were recorded on 500 MHz Joel 150 NMR machine. Chemical shifts were reported in ppm relative to tetramethyl silane (TMS) using $CDCl_3$. Gas chromatography analyses were realized on HP-6890-plus GC equipped with 30 m capillary column (HP-1).

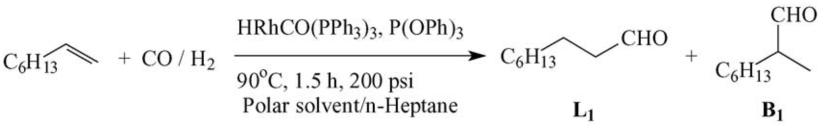
2.2. General procedure for biphasic hydroformylation of alkyl alkenes

A typical experimental procedure is as follow: 5.0 mmol of 1-octene, 0.005 mmol of $HRhCO(PPh_3)_3$ and 0.060 mmol of $P(OPh)_3$ were dissolved in a mixture of 2.0 ml of propylene carbonate and 4.0 ml of *n*-heptane and placed in the glass liner of a 45 ml Parr autoclave. The autoclave was purged three times with carbon monoxide, pressurized with 200 psi of $CO + H_2$ and then heated in an oil bath with temperature controller fixed at 90 °C. After 1.5 h the reaction mixture was cooled to room temperature and the biphasic reaction mixtures were separated. Aldehydes, present mainly in *n*-heptane phase, were identified by GC and GC-MS using *n*-decane as an internal standard. The ^1H and ^{13}C NMR of the products gave excellent spectral data compared to authentic samples.

3. Results and discussion

3.1. Effect of the type of polar solvents

Hydroformylation of 1-octene, chosen as a model substrate, into nonanal (**L_1** or *n*) and 2-methyl octanal (**B_1** or *i*) occurred smoothly at relatively mild conditions [90 °C, 200 psi ($CO/H_2 = 1{:}1$), 90 min], with $HRhCO(PPh_3)_3$ used as catalyst and $P(OPh)_3$ used as a ligand in a biphasic organic (thermomorphic) solvent system (Eq. (1)).



(1)

The most suitable biphasic solvent system, which led to high selectivity towards the desired linear products, included propylene carbonate and *n*-heptane. The total yield in aldehydes reached 84% with *n*/*i* ratio of 8.1 (88/11) and 10 (90/10) in *n*-heptane and propylene carbonate phases, respectively (Table 1,

Table 1
Biphasic hydroformylation of 1-octene. Effect of the type of polar solvent

Entry	Solvent mixture	*n*-Heptane		Polar solvent	
		Yield (%)	**B_1/L_1**	Yield (%)	**B_1/L_1**
1	DMF/*n*-heptane	45	18/82	35	17/83
2	DMSO/*n*-heptane	62	11/89	8	10/90
3	CH_3CN/*n*-heptane	52	12/88	25	11/89
4[a]	DMA/*n*-heptane	–	–	83	21/79
5	*N*-methylformamide/*n*-heptane	50	22/78	27	17/83
6	PC/*n*-heptane	65	11/89	12	10/90
7	Formamide/*n*-heptane	69	16/84	5	16/84
8[b]	Nitromethane/*n*-heptane	50	15/85	18	14/86

Reaction conditions: $HRhCO(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), polar solvent (2.0 ml), *n*-heptane (4.0 ml), 90 °C, 1.5 h, 1-octene (5.0 mmol), CO/H_2 (100/100 psi).

[a] No phase separation.

[b] 16 h.