CHINESE JOURNAL OF CATALYSIS
Volume 32, Issue 4, 2011
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Catal, 2011, 32: 566–571.

RESEARCH PAPER

Dicyclopentadiene Hydroformylation in an Aqueous/Organic Two Phase System in the Presence of a Cationic Surfactant

PI Xiaodong[1], ZHOU Yafen[1,2], ZHOU Limei[1,2], YUAN Maolin[1], LI Ruixiang[1], FU Haiyan[1,b],CHEN Hua[1,a]

[1]Key Laboratory of Green Chemistry and Technology of Ministry of Education, Department of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

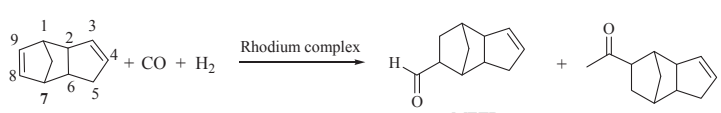
[2]College of Chemistry and Chemical Engineering, China West Normal University, Nanchong 637002, Sichuan, China

Abstract: Dicyclopentadiene (DCPD) hydroformylation catalyzed by the water soluble rhodium complex $RhCl(CO)(TPPTS)_2$ (TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$) was studied in an aqueous/organic two phase system containing a cationic surfactant. The effects of various reaction parameters such as reaction temperature, catalyst concentration, water soluble phosphine TPPTS or TPPDS ($C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$), and surfactant structure were examined. The catalytic activity was better with the ligand TPPTS than with TPPDS. The reaction was accelerated by the addition of the cationic surfactant $C_{16}H_{33}N(CH_3)_2C_nH_{2n+1}Br$ (n = 1, 8, 12, 16) but the accelerating effect was attenuated with an increase of the n value. In the presence of the surfactant, the DCPD conversion increased initially and then decreased as the rhodium concentration increased in the range of 0.05–5.00 mmol/L. The catalyst containing aqueous phase was reused four times without significant decrease in activity and regioselectivity.

Key words: aqueous/organic two phase system; dicyclopentadiene; hydroformylation; rhodium; surfactant

Dicyclopentadiene (DCPD) hydroformylation produces mono- and diformyl derivatives, which are hydrogenated to produce the corresponding carbinols. The carbinols are used as raw materials for agricultural chemicals, lubricating oil, plasticizer, and also as intermediate materials for pharmaceuticals and perfumes. For instance, the monocarbinols are valuable precursors for the synthesis of 4-homoisoteistane derivatives, which have powerful antiviral activity [1,2]. Since there are two unsaturated double bonds in its molecular structure, the products of DCPD hydroformylation are generally very complicated. Nevertheless, the greater reactivity of the more strained norbornenyl moiety probably directs the reaction mainly to the 8, 9 double bond [3]. Inamoto and coworkers [3] found that a rhodium triphenylphosphine complex can catalyze regioselective hydroformylation under relatively mild conditions, and obtained a mixture of 8- and 9-formyltricyclo [5,2,1,$0^{2,6}$]dec-3-ene (referred to as MFTD, Scheme 1) with over 80% yield.

Aqueous/organic two phase hydroformylation can facilitate the separation of the catalyst from the product. More importantly, the water solvent is environmentally friendly and meets the demand for green chemistry. Hydroformylation in the aqueous/organic two phase system has been extensively studied. The most successful industrial application is Rh-TPPTS (TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$) catalyzed propene hydroformylation, namely, the Ruhrchemie Rhône-Poulec (RCH/RP) process [4,5]. However, a relatively low activity was obtained with olefins with poor water solubility. There are several ways



Scheme 1. DCPD hydroformylation catalyzed by a rhodium phosphine complex.

Received 8 October 2010. Accepted 5 January 2011.
[a]Corresponding author. Tel: +86-28-85412904; Fax: +86-28-85412904; E-mail: scuhchen@163.com
[b]Corresponding author. Tel: +86-28-85412904; Fax: +86-28-85412904; E-mail: haijianfu@163.com
This work was supported by the National Natural Science Foundation of China (29792074) and the National Basic Research Program of China (973 Program, G2000048008).

DOI: 10.1016/S1872-2067(10)60182-9

to improve the water solubility of these olefins, such as adding co-solvent [6], co-ligand [7], amphiphilic phosphines [8–11], modified cyclodextrin [12–14], thermo-regulated phase transfer catalyst [15,16], and surfactants [17–25], to accelerate the aqueous/organic two phase hydroformylation. However, both the co-solvent and co-ligand inevitably lead to the loss of the catalyst. The synthesis of amphiphilic phosphine is usually tedious. The usage of modified cyclodextrin often provides poor regioselectivity. Therefore, the addition of a surfactant is more promising because this is usually commercially available and the synthesis method is relatively easy. Previously, we reported [21] that a cationic surfactant can effectively accelerate Rh-TPPTS catalyzed high olefin hydroformylation, especially when the surfactant concentration is higher than its critical micelle concentration (CMC). The reason was attributed to two factors: (1) the formation of the micelle increased the interfacial area of two phases and solubility of high olefins in the aqueous phase containing the rhodium complex; (2) the micelle cationic head groups were oriented towards the aqueous phase and formed a positively charged ion layer, which attracted active rhodium complex anion species to the interfacial layer from the aqueous solution. Thus, the catalyst was highly concentrated in the interfacial layer and could easily interact with olefin solubilized in the micelles. DCPD hydroformylation usually shows relatively low activity in an aqueous/organic two-phase system due to the poor solubility of DCPD in the water phase. The addition of a cationic surfactant is a feasible way to accelerate the reaction. However, only few research works in this area have been reported [26]. There is no report about the effect of the surfactant structure on DCPD hydroformylation. In this paper, we carried out DCPD hydroformylation catalyzed by the rhodium complex $RhCl(CO)(TPPTS)_2$ in an aqueous/organic two phase system. A strategy for accelerating the reaction by adding the cationic surfactants $C_{16}H_{33}N(CH_3)_2C_nH_{2n+1}Br$ (n = 1, 8, 12, 16) is presented. Various reaction factors, such as reaction temperature, catalyst concentration, type of ligand, and the surfactant structure were investigated.

1 Experimental

1.1 Materials

The water soluble ligands TPPTS and TPPDS ($C_6H_5P(m\text{-}C_6H_4SO_3Na)_2$), and the complex $RhCl(CO)(TPPTS)_2$ were prepared by following published methods [28]. Other reagents were purchased from commercial sources and used as received.

1.2 Surface tension experiment

The surface tension γ was determined by the maximum bubble pressure method at 28 °C. The pressure was measured with a precision digital pressure gauge (Sang Li Electronic Equipment Factory, Nanjing, China.)

1.3 Hydroformylation test

The hydroformylation reactions were performed in a 60 ml stainless steel autoclave with a magnetic stirrer. Known amounts of $RhCl(CO)(TPPTS)_2$, TPPTS, DCPD, surfactants, and water were added into the autoclave. After the autoclave was evacuated and purged with syngas three times, it was pressurized with the required volume of syngas (CO/H_2 = 1:1) and held at the desired temperature. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water to ambient temperature.

A HP 1890 series II gas chromatograph (Hewlett Packard, Palo Alto, CA) equipped with a flame ionization detector was used for product analysis. The separation was done on a SE-30 (30 m × 0.32 mm) fused silica capillary column.

2 Results and discussion

The product characterization was performed by the GC-MS instrument. Similarly to the results reported by Inamoto and coworkers, DCPD hydroformylation produced two major products, 8- and 9-formyltricyclo [5,2,1,$0^{2,6}$] dec-3-ene. Although the isomers of MFTD were separated on the gas chromatographic column, their individual identities could not be determined. We used the letter ‘E’ to denote the earlier isomer and ‘L’ to denote the later isomer according to the retention time of the isomers.

2.1 Effect of temperature

The preliminary experiment was carried out at 1.5 MPa initial syngas in the presence of 1.0 mmol/L cetyltrimethylammonium bromide (CTAB). The temperature range from 60 to 140 °C was investigated in order to test the effect of the temperature on DCPD hydroformylation. At temperatures lower than 80 °C, the DCPD conversion was very low after 1 h reaction time (Table 1, Entries 1 and 2). This increased with temperature increasing. The DCPD was almost completely converted at 120 °C. However, at this temperature the organic phase exhibited a light yellow color (Table 1, Entry 4), which indicated a loss of the rhodium complex into the organic phase. Therefore, the reaction temperature was set at 100 °C in the following experiments.

2.2 Effect of the rhodium complex concentration

The effect of rhodium complex concentration on DCPD hydroformylation was tested in the range of 0.05–5.00 mmol/L. The results are shown in Table 2. With the rhodium complex