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Aqueous Biphasic Hydroformylation of Oleyl Alcohol Catalyzed by Thermoregulated Rhodium Complex

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Abstract: The aqueous biphasic hydroformylation of oleyl alcohol was achieved under thermoregulated phase transfer catalysis (TRPTC) conditions with $Rh(acac)(CO)_2$ $Ph_2P[p\text{-}C_6H_4(OCH_2CH_2)_{25}OH]$ (PETPP) complex catalyst formed *in situ*. The aldehyde yield reached 81.2% within 6 hrs under 140℃ and 5.0 MPa (CO/H_2,1/1) and the separated catalysts dissolved in the aqueous phase could be reused for 3 times without evident changes in activity.

Keywords: Rhodium, hydroformylation, oleyl alcohol, TRPTC.

Hydroformylation products of oleyl alcohol (OA) had been practically employed as plasticizers, urethane foams and lubricants[1]. Since OA was absolutely insoluble in water, extremely low conversion was achieved with $HRh(CO)(TPPTS)_3$ as catalyst in aqueous/organic two phase system[2]. To overcome this constraint, Hanson[2] used $HRh(CO)(TPPTS)_3$ as catalyst with the addition of surfactant or co-solvent and reasonable aldehyde yield was achieved. Moreover, a supported aqueous phase (SAP) Rh/TPPTS complex catalyst was introduced and obtained good result[3]. Utilizing homogeneous oil-soluble $P[m\text{-}C_6H_4SO_3NH\text{-}(i\text{-}C_8H_{17})_3]_3$ /2-ethyl hexabasic rhodium complex as catalyst, Henkel AG had built a pilot-plant for the hydroformylation of OA [4]. Jin[5] *et al.* proposed concept of thermoregulated phase transfer catalysis (TRPTC) based on ethoxylated tris(*p*-hydroxyphenyl) phosphines which exibited inverse temperature dependent water solubility “cloud point” just as in the case of nonionic surfactant. The Rh/PETPP complex catalyst is soluble in aqueous phase at a lower temperature and can transfer into the organic phase at higher temperature as “cloud point”. At the reaction temperature above the cloud point, the catalyst resides in the organic phase and thus catalyzes the reaction proceeding homogeneously. as soon as the reaction completes and the system cools to a temperature lower than the cloud point, the catalyst returns to aqueous phase. Thus, TRPTC provides a meaningful breakthrough to the limitation of low reaction rates of poor water-soluble substrates. The TRPTC had been successfully used in the aqueous biphasic hydroformylation of linear higher olefins[6]. This report extented TRPTC to

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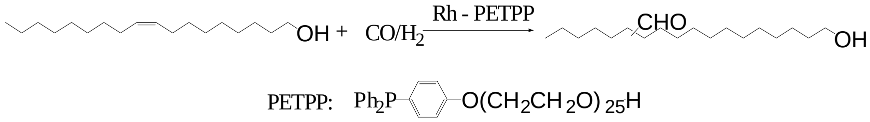
the aqueous biphasic hydroformylation of OA, although OA was absolutely insoluble in water (**Scheme 1**).

Scheme 1



The results of the aqueous biphasic hydroformylation of OA catalyzed by Rh/PETPP complex were summarized in **Table 1**. At optimal temperature 140℃, the aldehyde yield was as high as 81.2% (entry 2); when the temperature reached 160℃, the aldehyde yield decreased to 75.4% (entry 3). While increasing the syngas (CO/H_2, 1/1) pressure significant increase in the aldehyde yield was observed (entries 2,4,5); but when the total pressure changed from 5.0 MPa to 6.0 MPa, only a slight increase of the aldehyde yield was observed (entry 6). A significant increase in the aldehyde yield was achieved by running the reaction at a higher P/Rh ratio (Entry 8); and when the P/Rh molecular ratio changed from 6 to 10, the aldehyde yield slightly increased from 79.2% to 81.2%; However, further increase of the P/Rh ratio to 14/1, the aldehyde yield decreased slightly to 80.9% (entry 9). Finally, A small increase in the aldehyde yield was obtained by running the reaction at a higher concentration of rhodium (entries 11,2,10).

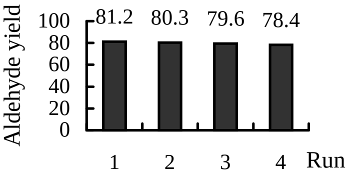
The catalyst-contained aqueous phase could be separated by simple decantation and reused directly in the next catalytic run. The results in **Figure 1** showed the recycle experiment results of the Rh/PETPP complex catalysts. After four successive reaction runs, the yield of aldehyde still remained as high as 78.4%. Thus satisfactory catalytic stability was achieved.

Table 1 Aqueous biphasic hydroformylation of oleyl alcohol based on Rh/PETPP complex

Entry	Temperature (°C)	P(CO/H_2, 1:1)(MPa)	P/Rh (mol/mol)	OA/Rh (mol/mol)	Aldehyde Yields(%)
1	120	5.0	10/1	1000/1	69.8
2	140	5.0	10/1	1000/1	81.2
3	160	5.0	10/1	1000/1	75.4
4	140	3.0	10/1	1000/1	58.9
5	140	4.0	10/1	1000/1	73.0
6	140	6.0	10/1	1000/1	81.8
7	140	5.0	3/1	1000/1	50.0
8	140	5.0	6/1	1000/1	79.2
9	140	5.0	14/1	1000/1	80.9
10	140	5.0	10/1	500/1	83.4
11	140	5.0	10/1	2000/1	72.8

Reaction conditions: $RhCl_3.3H_2O$, PETPP-M, $V_{H2O}/V_{heptane}$ =1:1, $V_{OA}/V_{heptane}$ =1:2, 6 hrs

Figure 1 Aqueous biphasic hydroformylation of oleyl alcohol based on Rh/PETPP complex



In conclusion, although OA was absolutely insoluble in water, considerable high aldehyde yield was obtained.So it was presumed that this reaction proceeds effectively and steadily can only be based upon the TRPTC concepts. The above-mentioned good results convincingly proved that TRPTC is a general qualified model for aqueous biphasic catalysis of poorly water-soluble substrate; it also directed a novel and effectively separable two-phase catalytic system for hydroformylation of OA. This catalytic system also might be regarded as a promising avenue for further exploration of hydroformylation of OA on a commercially realistic scale.

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