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Hydroformylation of Oleyl Alcohol Catalyzed by Rh-OPGPP Complex

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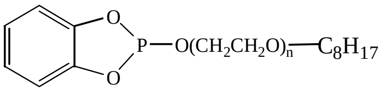
Abstract: Polyether-tailored phosphite modified rhodium complex formed *in situ* was highly active in the hydroformylation of oleyl alcohol in nonaqueous phosphite/heptane system where the phosphite acted both as the ligand and the second phase. This catalyst was easily separated by simple decantation and can be used for five times with only a slight decrease in activity.

Keywords: Phosphite, hydroformylation, oleyl alcohol, nonaqueous biphasic catalysis.

Hydroformylation products of oleyl alcohol (OA) have been practically employed as plasticizers, urethane foams and lubricants[1]. Since OA is absolutely insoluble in water, extremely low conversion was achieved with $HRh(CO)(TPPTS)_3$ as catalyst in aqueous / organic two phase system [TPPTS: $(m\text{-}NaSO_3\text{-}C_6H_4)_3P$][2]. To overcome this constraint, Hanson used $HRh(CO)(TPPTS)_3$ as catalyst with the addition of surfactant and co-solvent and reasonable yield of the aldehyde was achieved[2]. Moreover, a supported aqueous phase (SAP) Rh/TPPTS complex catalyst was introduced and good result was obtained[3]. Utilizing homogeneous oil-soluble $P[m\text{-}C_6H_4SO_3NH(i\text{-}C_8H_{17})_3]_3$/2-ethylhexabasic rhodium complex as catalyst, Henkel AG had built a pilot-plant for the hydroformylation of OA[4].

Scheme 1



1. **OPGPP**, n=19
2. **OPGPP**, n=57

In our previous study, water-soluble $Rh(acac)(CO)_2$-OPGPP (**Scheme 1**) complex (OPGPP, octylpolyglycol-phenylene-phosphite) has been demonstrated to be an efficient thermoregulated phase transfer catalyst for aqueous biphasic hydroformylation of styrene[5]. The activity is considerably losed when the catalyst was reused, mainly due to the sensibility of the O-P bond in OPGPP to water.

To avoid the hydrolysis of OPGPP, a nonaqueous catalytic system was attempted. Interestingly, we found that when OPGPP/heptane biphasic system was used, under 5.0 MPa, 140°C, OPGPP/ $Rh(acac)(CO)_2$ (mol/mol):80, Rh/Substrate (mol/mol): 1/1000, 6hrs conditions, the catalysts has showed good activity in the hydroformylation of OA.

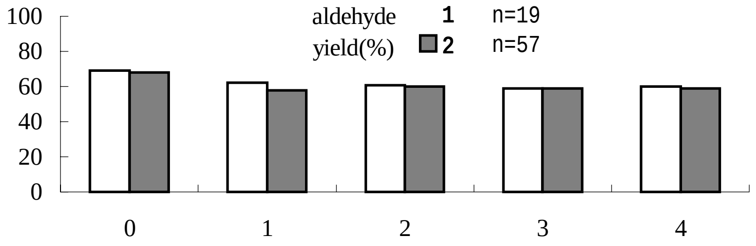
After reaction, the lower OPGPP phase appears to be brown mash or wax and the upper heptane phase was colorless clear liquid. The lower brown phase containing the catalyst was separated by simple decantation and used directly in the recycling experiments. After five reaction runs (see **Figure 1**), the yield of aldehyde still remained 60% or so.

Table 1 Solubility of OPGPP at different temperatures

OPGPP	solvent	Temperature(°C)	Ligand solubility
1: n=19	heptane	16	0.31
1: n=19	heptane	90	0.55
2: n=57	heptane	16	0.006
2: n=57	heptane	90	0.972

Although OPGPP with different PEG chains have different solubility in heptane (see **Table 1)**, the aldehyde yields are quite similar (see **Figure 1**). This indicates that the reaction did not proceed in the organic phase. On the other hand, it was a common concept that in the ionic liquid involved biphasic system the reaction proceeded in the lower ionic liquid phase[6]. We assumed that probably the reaction occurred in the OPGPP phase or on the interface of OPGPP and heptane. Further studies to clarify this problem are now under investigation.

Figure 1 Two-phase hydroformylation of oleyl alcohol catalyzed by Rh-OPGPP complex



Acknowledgments

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