

## Polyether-phosphinite for One-phase Catalysis Coupled with Two-phase Separation

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**Abstract:** Polyether moiety was introduced to the phosphinite and the phosphinite modified rhodium complex formed *in situ* was highly active in the hydroformylation of higher olefins in organic monophasic system. After reaction, on cooling to room temperature, the catalyst could precipitate out from organic phase and was easily separated by decantation and reused six times without obvious decreasing in activity.

**Keyword:** Phosphinite, hydroformylation, higher olefins, catalyst separation.

Functionalized polymers and oligomers provide a versatile route to prepare supports for use in catalytic chemistry. Insoluble functional polymeric materials have often been used because of their facile separation from the reaction mixtures, while decrease in activity compared with homogeneous catalysis and loss of catalyst in the process would be inevitably encountered in the pilot application<sup>1</sup>. Transition-metal catalysts with soluble supports are the highlight in the recent literatures, due to the characteristic advantage of one-phase catalysis and easy separation of the catalysts from the mixture by various procedures<sup>2-4</sup>.

Some polyether-derived triphenylphosphine ligands which possess the thermo-regulated phase transfer property reported by our group have been successfully applied in the aqueous-organic biphasic hydroformylation of higher olefins<sup>5-9</sup>.

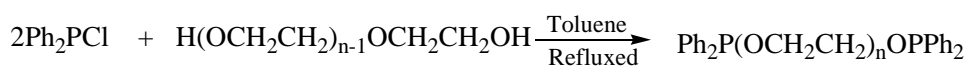
In this paper, we reported a novel polyether-phosphinite and its rhodium complexes in the application of organic monophasic hydroformylation of higher olefins. The catalytic system was remarkably characterized with high catalytic reactivity and facile separation of the catalyst. The above-mentioned catalytic system is especially preferred for the reaction in which the substrate or catalyst is sensitive to water.

The polyether phosphinite was synthesized by reaction of diphenylphosphine chloride and polyethylene glycol (see **Scheme 1**), and it was interestingly observed that phosphines possessing long-chain polyether could precipitate quantitatively from the solution at room temperature while they dissolve in the hot organic solvents.

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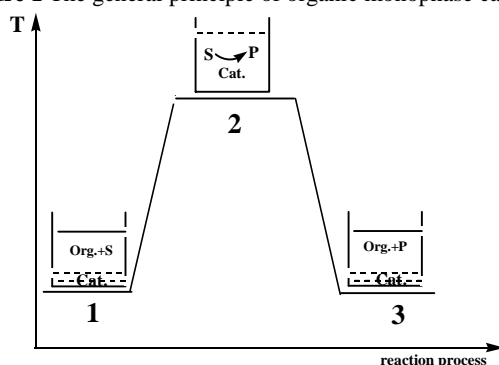
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## Scheme 1



This phenomenon triggered us to explore a new catalytic system termed as organic monophase catalysis, and the hydroformylation of higher olefins was chosen as a model reaction. The diphenylphosphine terminated PEG derivatives were used as ligands in the rhodium catalysed hydroformylation of 1-decene. The phosphinite derived from

**Figure 1** The general principle of organic monophase catalysis



S: substrate, P: product, Cat.: catalyst, Org.: organic solvent, T: temperature  
1: before reaction, 2: during reaction, 3: after reaction

PEG 3000 was specifically investigated in the catalytic reaction. The general principle of organic monophase catalysis is illustrated in **Figure 1**. Before reaction (at room temperature), the catalyst is insoluble in organic solvent. During reaction, with increasing of reaction temperature, the catalyst becomes soluble in organic solvent and the whole system is homogeneous. After reaction, when cooling to the room temperature, the catalyst could precipitate out from organic phase. Thus, the catalyst could be easily separated from the product by decantation.

From the results shown in **Table 1**, 1-decene was hydroformylated in toluene with a high conversion at 80°C or higher temperature. After reaction, the separated organic phase by decantation was in yellow color, indicating great loss of the catalyst in the organic phase. The catalyst separation can be improved greatly with heptane as solvent than with toluene. A conversion of more than 93% in heptane could also be obtained at 130°C. The rose catalyst precipitated in the bottom of the autoclave from colorless organic phase of heptane.

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**Table 1** Hydroformylation of 1-decene catalysed by polyether-phosphinite/Rh catalyst

run	solvent	Reaction temperature (°C)	Conversion (%)	Aldehyde yield (%)	Aldehyde n/iso
1	toluene	50	48.6	48.6	1.32
2	toluene	80	89.3	89.3	0.98
3	toluene	100	98.5	94.2	0.74
4	heptane	100	88.6	88.6	0.68
5	heptane	130	93.4	87.0	0.45

Reaction conditions: polyether-phosphinite (n=68)/Rh(acac)(CO)<sub>2</sub>=13, 1-decene /Rh=1000, syngas pressure 5.0 MPa, 1-decene 2.0 ml, solvent 4.0 ml, 0.3 ml dodecane as interior standard, reaction time 6 h.

The above catalyst has also been applied in the hydroformylation of other higher olefins (1-hexene, 1-octene, 1-dodecene, 1-tetradecene) as shown in **Table 2**. Under the same conditions, more than 90% of conversions were obtained with 85% higher of aldehyde yield. These results suggest that the above catalyst are highly active in the hydroformylation of long chain  $\alpha$ -olefins.

**Table 2** Polyether-phosphinite/Rh catalyzed hydroformylation of different higher olefins

run	substrate	Conversion (%)	Aldehyde yield (%)	Aldehyde n/iso
6	1-hexene	97.3	89.6	0.73
7	1-octene	95.0	89.1	0.61
8	1-dodecene	93.0	87.0	0.43
9	1-tetradecene	92.1	85.0	0.43

Reaction conditions: PEG-phosphinite (n=68) /Rh(acac)(CO)<sub>2</sub>=13, olefin/Rh=1000, syngas pressure 5.0 MPa, olefin 2.0 ml, heptane 4.0 ml, 0.3 ml dodecane as interior standard, 130°C, reaction time 6 h.

After reaction, the catalyst precipitated quantitatively at room temperature, hence the catalyst could be easily separated from mixtures by simple decantation and be applied in the consecutive reaction runs (as shown in **Table 3**). The catalyst can be reused six times without great decrease in activity.

**Table 3** Recycling of the polyether-phosphinite/Rh catalyst in the hydroformylation of 1-decene

run	consecutive runs	Conversion (%)	Aldehyde yield (%)	Aldehyde n/iso
10	1	93.4	87.0	0.45
11	2	93.2	88.0	0.46
12	3	91.3	88.8	0.45
13	4	89.3	87.1	0.46
14	5	89.0	87.3	0.48
15	6	89.0	87.0	0.50
16	7	85.6	81.0	0.54

Reaction conditions: polyether-phosphinite (n=68) /Rh(acac)(CO)<sub>2</sub>=13, olefin /Rh =1000, syngas Pressure 5.0 MPa, 1-decene 2.0 ml, heptane 4.0 ml, 0.3 ml dodecane as interior standard, 130°C, reaction time 6 h.

The polyether-phosphinite/Rh complex system formed *in situ* is active in the hydroformylation of higher olefins in the organic monophase system. The catalytic

system was characterized by homogeneous catalysis coupled with convenient two-phase separation. The catalysts can be directly reused without remarkable loss of their catalytic activity. The reaction mechanism of the catalytic system is in progress.

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