Hydroformylation of Mixed Octenes Using Rhodium–Bulky Phosphonite Complexes with Excellent Catalytic Activity and Stability

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Rhodium catalyst liganded with tetrakis-(2,4-di-*t*-butyl-phenyl)-4,4′-biphenylphosphonite exhibited an excellent catalytic activity as well as stability for the hydroformylation of mixed olefins, especially butene dimer.

Hydroformylation products, such as C_9-aldehydes and C_9-alcohols, from the mixture of isomeric octenes have attracted much attention owing to their high performance in solvents, plasticizers, and various detergent applications.[1–3] It is well known that the olefin hydroformylation employs homogeneous complex catalysts such as Group VIII transition metal complexes containing phosphorous ligands in the presence of hydrogen and carbon monoxide.[4] Typically, Rh complexes have been considered as an excellent catalyst for the hydrofomylation owing to high activity, mild reaction conditions, easy recovery of the catalyst, and high yield of n/i ratio of products.[5] The ligand in the complex gives substantial influence on catalytic activity and various kinds of phosphorous compounds have been used as the ligands. In case of lower olefins and long-chain α-olefins, the traditional phosphine ligands such as trialkyl or triarylphosphine ligands have been widely used in the hydroformylation. However, it has been reported that the catalyst containing the phosphine ligands exhibits a markedly low activity in the hydroformylation of the mixture of internal and/or branched olefin which can be obtained through oligomerization of low olefin.[6] Recently, a Rh catalyst modified with triphenylphosphine oxide (TPPO) has been commercialized for hydroformylation of mixed olefins.[7] However, the addition of phosphine is necessary to stabilize the rhodium catalyst before the distillation step for catalyst recovery. Various kinds of phosphite compounds such as triorganophosphites and diorganophosphites have also been proposed as the ligands for the catalyst design.[8,9] In these cases, the stability of the phosphite compounds has not been always satisfied in the catalytic process because it is requested to maintain its catalytic activity for a long term in industry.

In the present work, we aimed to develop a new ligand to increase catalyst stability as well as to maximize activity and selectivity. A rhodium complex with tetrakis-(2,4-di-*t*-butylphenyl)-4,4′-biphenylphosphonite ligand (TBPBPP) was selected and it exhibited excellent activity and stability for hydroformylation of mixed octenes obtained via butene dimerization.

A C_4 fraction obtained by removing butadiene and isobutene from a naphtha cracker was dimerized in a fixed bed reactor including Ni/Al_2O_3 catalyst under 50 bar at 70 °C.[10,11] After reaction, the product containing C_4-, C_8-, and C_{12} fraction was distilled to separate a C_8-olefin mixture, which was composed with 11.0 wt % of dimethylhexenes, 68.3 wt % of methylhep-

tenes, and 20.7 wt % of normal octenes. $Rh_2(CH_3CO_2)_4$ was added to a SUS-316 autoclave reactor (300 mL) containing 100 mL of the mixture of octenes, giving 13 ppm of rhodium concentration. A phosphorous compound such as tri-*t*-butyl phosphine (TBP), triphenylphosphine (TPP), tris(2,4-di-*t*-butylphenyl phosphite (TDTBPP), triphenylphosphine oxide (TPPO), tertiary bisphenyl dioxide (TBPDO), or TBPBPP was added into the autoclave. Subsequently, the autoclave was sealed and flushed with nitrogen gas. The syn-gas ($CO/H_2 = 1$) was pressurized up to 30 bar in the reactor, and then released to atmospheric pressure. This pressurized and released process was repeated three times, and then the reactor was heated to 140 °C. Immediately after the temperature reached to 140 °C, the syn-gas was introduced under pressure to bring the total pressure of 160 bar. The reactor was kept at that temperature for 2 h, and the syn-gas was filled up from a reservoir to maintain the pressure of 160 bar. After the completion of the reaction, the resulting products were analyzed by gas chromatography. The reaction solution was distilled in nitrogen atmosphere under a pressure of 2–3 mmHg at 120 °C to distill the aldehydes and alcohols. The amount of remaining rhodium in distillate was determined by elemental analysis. The hydroformylation reaction was carried out in the same manner as in the above procedure except that the recycled catalyst was used instead of fresh catalyst.

The octene conversion and product selectivity of the various kinds of Rh-based catalysts for the hydroformylation are listed in Table 1. The octene conversions over the Rh catalysts containing TBP and TPP are very low. Although the Rh–TPP catalyst has been used in commercial process for hydroformylation of propylene to produce butyraldehydes,[12,13] it shows low activity (40.5%) in the hydroformylation of the mixture of octenes in the present work. This is probably because the mixture of octenes is used as obtained from the butene dimerization, which consist of internal and/or branched olefins. Steric effect is believed to be very important factor in the hydroformylation of alkenes over the Rh-based complexes containing phosphorous compounds.[14] The rate of hydroformylation falls with increasing steric hindrance in the ligand and the substrate. The reactivity of substrates decreases in the series 1-alkenes > substituted 1-alkenes > internal alkenes.[14] However, even though the TDTBPP (phosphite), TBPDO (phosphine oxide), and TBPBPP (phosphonite) ligands are very bulky, the Rh-based catalysts containing such a bulky ligand exhibit the similar octene conversion and C_9 products yield to those of Rh-catalysts with TPPO ligand and Rh-catalyst without ligand, as shown in Table 1. These results indicate that the binding strength between Rh and ligand is also important for the catalytic activity. In cases of Rh catalyst systems with the phosphite, phosphine oxide, or phosphonite, it is

Table 1. Conversion and selectivity of hydroformylation

Ligand[a]	Conversion /%	Yield /%		
		C_9-aldehyde	C_9-alcohol	HBPBP[b]
-	88.2	80.4	7.8	0
TBP	29.5	25.4	4.1	0
TPP	40.5	36.6	3.9	0
TDTBPP	87.0	81.4	5.6	0
TPPO	89.0	79.3	9.6	0.1
TBDO	86.1	76.5	8.6	1.0
TBPBPP	85.6	83.0	2.6	1.0

[a]Amount of ligand: P/Rh = 20. [b]high boiling point byproduct.

relatively easy to coordinate with Rh for mixed octenes because of the relatively low stability of Rh-these ligands. Consequently, the low activity of Rh-phosphine systems such as Rh–TBP and Rh–TPP is probably due to high stability of Rh–P species that causes to prevent coordination with Rh for mixed octenes.

In addition to the catalytic activity, it is necessary to reduce the amount of Rh loss during distillation of hydroformylation product. Because the hydroformylation products are distilled at high temperature in order to recover Rh-catalyst system from hydroformylation products, the amount of Rh loss during this process is very important factor of production cost. The Rh loss may be due to decomposition of Rh-ligand system during the distillation. Table 2 shows the hydroformylation results obtained by using the catalysts recovered by distillation of products. The Rh concentrations in Table 2 indicate the amount of Rh loss during the distillation process. The C_9 yields over the Rh-based catalysts containing TDTBPP and TBDO decrease drastically with recycling time of the catalysts. This is similar to the trend of Rh catalyst without ligand. The C_9 yield over the Rh-TBPBPP catalyst, however, is not significantly changed upon the catalyst recycle. These results are attributed to the stability of the Rh-based catalysts during the product distillation. The Rh-TBPBPP catalyst exhibits much less amount of Rh loss during distillation than

Table 2. Yield of hydroformylation and Rh loss during distillation by using the recycled catalysts

Ligand[a]	Catalyst	C_9-al + C_9-ol yield /%	Rh concentration in distillate /ppm[b]
-	fresh	88.2	0.158
	recycled	83.6	0.167
	recycled twice	78.8	0.180
TDTBPP	fresh	87.0	0.089
	recycled	82.1	0.073
	recycled twice	80.1	0.115
TBDO	fresh	85.1	0.110
	recycled	83.2	0.171
	recycled twice	80.6	0.216
TBPBPP	fresh	85.6	0.036
	recycled	85.3	0.043
	recycled twice	84.1	0.041

[a]Amount of ligand in fresh catalyst: P/Rh = 20; No new ligand was added in the second and third cycle. [b]Distillation condition: 2–3 mmHg; 120 °C.
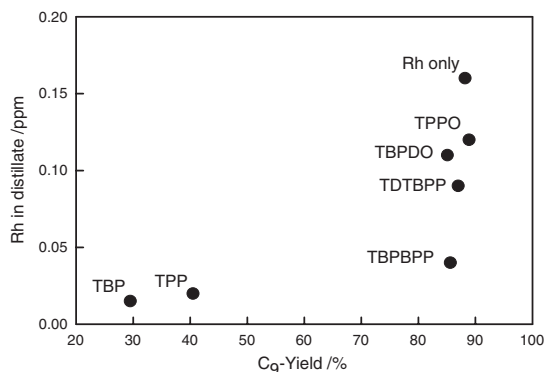
Figure 1. Relation between the catalytic activity and Rh concentration in distillates of the Rh-based catalysts containing various kinds of ligands.

those of other catalysts, as shown in Table 2.

The relation between the catalytic activity and catalytic stability of the various Rh-based catalysts is shown in Figure 1. The catalyst with high C_9 yield and low Rh concentration in distillate is believed to be an excellent one for the hydroformylation of mixed octenes. Figure 1 clearly indicates that the Rh–TBPBPP catalyst is most effective for the hydroformylation of mixed octenes in the present work.

In conclusion, the Rh-based catalyst containing TBPBPP ligand exhibits an excellent catalytic activity as well as stability for the hydroformylation of mixed olefins in the present work, indicating the nature of ligand is very important for the catalyst design.

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