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Studies on the Recycling Efficiency of Thermoregulated Phase-separable Rh/PETPP Complex Catalyst

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Abstract: Effects on the recycling efficiency of thermoregulated phase-separable Rh/PETPP (P-[*p*-$C_6H_4O(CH_2CH_2O)_nH]_3$, N=3n) complex catalyst involved in hydroformylation of 1-decene are for the first time presented. It was found that the loss of Rh is dependent greatly on the composition of phosphine ligand PETPP and the organic solvent employed in the reaction.

Keywords: Thermoregulated phase-separable catalysis (TPSC), hydroformylation, nonionic phosphine ligand, rhodium.

The liquid/liquid biphasic catalysis has been a preferable strategy due to its combination with the advantages of homogeneous and heterogeneous catalysis[1-2]. In our previous work, the characteristic of critical solution temperature (CST) of nonionic phosphine ligand PETPP in toluene was found and applied in the hydroformylation of higher olefins[3]. Based on the property of CST of phosphine ligand, a novel biphasic catalytic process termed as thermoregulated phase-separable catalysis (TPSC) has been proposed[4]. The general principle can be described as follows: at room temperature (T<CST), the catalyst is insoluble in organic solvent. When heating to T>CST, the catalyst would be soluble in organic solvent and the whole system turned to be homogeneous. At the reaction temperature (T>CST), the reaction proceeds homogeneously. After completion of the reaction, on cooling to the room temperature (T<CST), the catalyst would precipitate out from the organic phase. Thus, by decantation the catalyst could be easily separated from the products and reused. Under the conditions of T=130°C, P=6.0 MPa (CO/H_2=1:1), $RhCl_3=5\times10^{-6}$mol, substrate/Rh=1000, PETPP(N=18)/Rh=10 (PETPP: P-[*p*-$C_6H_4O(CH_2CH_2O)_nH]_3$,N=3n), toluene=2.0 mL, reaction time=4 h., the conversion of 1-decene and the yield of aldehyde are 98.7% and 96.0%, respectively. In addition, the turnover frequency (TOF) which can indicate the catalytic activity of the reaction is 240 h^{-1}. After reaction, the upper layer organic phase was separated by decantation and analyzed. The loss of Rh in the organic phase was 1.26% (w%). With the aim to further decrease the loss of Rh and improve the recycling efficiency of thermoregulated phase-separable Rh/PETPP complex catalyst, which was employed in the hydroformylation of 1-decene, in this paper the effects of the average value of N, the

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distribution of N and the organic solvents are firstly discussed.

It is well known that $RhCl_3$ used as the catalyst precursor is almost insoluble in toluene at room temperature. Therefore, the loss of Rh is mainly due to its coordination with phosphine ligand PETPP. However, different average value of N and its distribution would endow PETPP with different solubility in toluene at room temperature, so the loss of Rh will be affected by the average value of N and its distribution.

Effect of the average value of N on the loss of Rh was investigated (see **Table 1**). With increasing of the N value, the loss of rhodium increases. Thus, the optimized average chain length of PETPP is N=18.

Table 1 Effect of average value of N on the loss of Rh

Average value of N	18	24	34	42
Loss of Rh (w %)	1.26	1.29	1.65	1.80

Figure 1 Effect of distribution of N

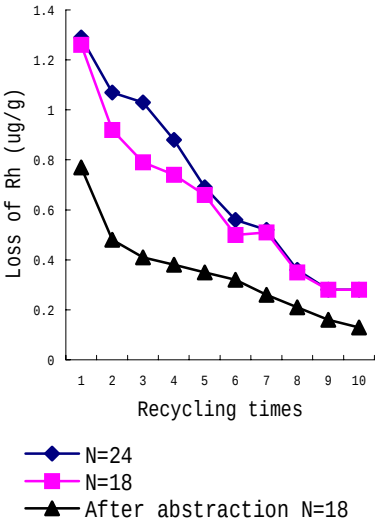
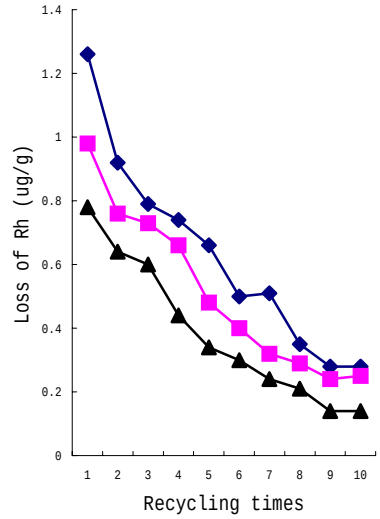


Figure 2 Effect of organic solvent



---Δ--toluene/heptane=1:10(volume ratio)

As we have known that thermoregulated phase-separable phosphine ligand PETPP was synthesized by the ethoxylation of P-[*p*-C_6H_4OH]$_3$, so it is a mixture of ligands with different values of N. Considering this condition, the effect of distribution of N on the loss of Rh is also studied (see **Figure 1**). After several times abstraction of PETPP with anhydrous toluene, the average value of N is changed from 24 to 18 and the distribution of N becomes narrower. From the results in **Figure 1** we can see that PETPP with the narrow distribution of N benefits the recycling efficiency of Rh, although the average

value of N is identical.

To further improve the recycling efficiency of catalyst, another approach has been developed to use a mixed solvent of toluene and heptane. By adding heptane into the solvent, the solubility of PETPP becomes considerable lower and the loss of Rh decreases evidently (see **Figure 2**).

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