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Thermoregulated Phase-separable $Ru_3(CO)_{12}$/PETPP Complex Catalyst for Hydrogenation of Styrene

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Abstract: Thermoregulated phase-separable $Ru_3(CO)_{12}$/PETPP (PETPP=P[p-C_6H_4O $(CH_2CH_2O)_n$ H]$_3$, n=6) complex catalyst was first applied in the hydrogenation of styrene. Under the conditions: $P(H_2)$=2.0MPa, T=90°C, styrene could be completely transferred and the yield of ethylbenzene reached up to 99.5%. After simple decantation, the catalyst could be reused for ten times without decreasing in activity.

Keywords: Thermoregulated phase-separable catalysis, hydrogenation, styrene, ruthenium.

The basic problem in homogeneous catalysis is the separation of catalyst from the reaction mixtures. To overcome this drawback, a number of methods have been developed. One of them is to attach homogeneous catalyst to supports [1]. An alternative and well used approach involves liquid/liquid biphasic catalysis in which the catalyst and product reside in different phases and separation of the products is achieved simply by phase separation[2]. Recently, a concept of thermoregulated phase transfer catalysis has been developed by Jin[3,4].

Based on the critical solution temperature (CST) of nonionic tensioactive phosphine ligand in toluene, a novel liquid/liquid biphase catalytic concept termed as thermoregulated phase-separable catalysis(TPSC) has been proposed and applied in the hydroformylation of higher olefins[5,6].

Here we reported the hydrogenation of styrene catalyzed by thermoregulated phase separable $Ru_3(CO)_{12}$/PETPP complex catalyst. Under the conditions: $P(H_2)$=2.0MPa, T=90°C, catalyst/ substrate(mol/mol)=1/1000, 3 hrs, the $Ru_3(CO)_{12}$/PETPP complex catalysts have shown good activity (**Table 1**). Compared with other catalysts, $Ru_3(CO)_{12}$/ PETPP complex showed the same catalytic activity with the lipophilic $Ru_3(CO)_9(TPP)_3$, while higher than the hydrophilic $Ru_3(CO)_9(TPPTS)_3$ and $Ru_3(CO)_9(TPPMS)_3$ (**Table 2**). At room temperature (T<CST), the $Ru_3(CO)_{12}$/ PETPP complex catalyst is insoluble in toluene. When heated to T>CST, the catalyst is soluble in toluene. At the reaction temperature (T>CST), the reaction proceeds homogeneously. After completion of the reaction, on cooling to room temperature (T<CST), the catalyst precipitates from toluene. Thus, the catalyst was separated by simple decantation and used directly in the recycling

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experiments. After ten reaction runs (**Figure** 1), the yield of ethylbenzene remained more than 95%.

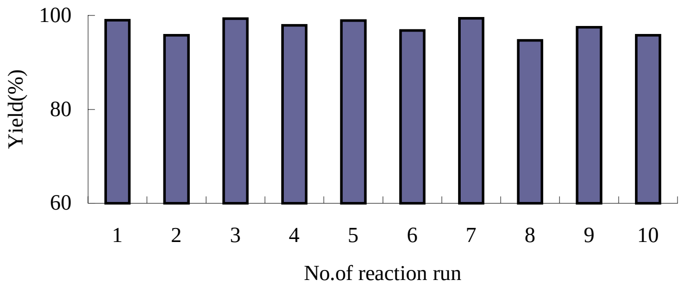
Table 1 Effect of temperature on the hydrogenation of styrene with $Ru_3(CO)_{12}$/PETPP

Temperature（°C）	Conversion(%)	Yield(%)	Turnover(h^{-1})
90	100.0	99.5	332
80	93.7	93.1	310
70	60.4	60.1	200
60	40.1	40.0	133

Table 2 Effect of different P/Ru catalyst on the hydrogenation of styrene

Catalyst	Conversion(%)	Yield(%)	Turnover(h^{-1})
$Ru_3(CO)_9(TPP)_3$	96.6	95.8	319
$Ru_3(CO)_9(TPPMS)_3$	76.8	76.4	255
$Ru_3(CO)_9(TPPTS)_3$	48.2	48.0	160
$Ru_3(CO)_{12}$/PETPP	100.0	99.5	332

Figure 1 Recycling efficiency of $Ru_3(CO)_{12}$/PETPP complex catalyst



In conclusion, $Ru_3(CO)_{12}$/PETPP complex catalyst is active in the hydrogenation of styrene. The TPSC was characterized by homogeneous catalysis coupled with two-phase separation. The catalyst could be reused without regeneration and loss of catalytic activity.

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References

1. H. H. Lamb, B. C. Gates, H. Knozinger, *Angew. Chem. Int. Ed. Engl*., **1998**, *27*, 1127.
2. W. A. Herrmann, C. W. Kohlpainter, *Angew. Chem. Int. Ed. Engl*., **1993**, *32*, 1524.
3. Z. L. Jin, X. L. Zheng, B. Fell, *J. Mol. Catal. A: Chem*., **1997**, *116*, 55.
4. R. F. Chen, X. Z. Liu, Z. L. Jin, *J. Organomet. Chem.*, **1998**, *571*, 201.
5. Y. H. Wang, J. Y. Jiang, R. Zhang, X. H. Liu, Z. L. Jin, *J. Mol. Catal. A: Chem*., **2000**, *157*, 111.
6. Y. H. Wang, J. Y. Jiang, X. W. Wu, F. Cheng, Z. L. Jin, *Catal. Lett*., in press.

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