

POLYMER SUPPORT EFFECTS OF METAL COMPLEXES FOR CATALYSIS*

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Abstract In the course of investigating the catalytic behavior of metal complexes for ring opening metathesis polymerization of cycloolefins, metathesis, hydroformylation and selective hydrogenation of olefins experimental results time and again indicate the presence of effects of macromolecular supports—the utilization of macromolecular supports increases obviously the activity, selectivity, and stability of the catalysts and so as to increase the conversion of substrates, yields of reactions, properties of formed polymers and so on. Discussed these effects on the basis of the authors' experiments.

Keywords Polymer supported catalysts; Metal complexes; Support effects

INTRODUCTION

In the past 30-odd years synthesis by the aid of polymers has made dramatic and mighty advances. The outstanding achievements reached in the areas of Merrifield solid-phase peptide synthesis^[1], polymer immobilized enzymes^[2] polymer-supported metal complex catalysts^[3], ligand-exchange chromatography^[4] etc. demonstrated undoubtedly the broad and brilliant prospects of polymer-mediated synthesis.

We have been doing research on polymer-supported metal complex catalysts for catalytic organic synthesis (hydroformylation, selective hydrogenation, metathesis of olefins etc) and polymerization (ring opening metathesis polymerization of cycloolefins, cationic polymerization etc.) since the late seventies. Time after time we observed the effects of polymer supports of metal complex catalysts—immobilizing homogeneous metal complex catalysts on the tailor-made polymer supports increases distinctly the catalysts' activity, selectivity, stability, reusability and so on. It will be of great benefit if these effects could be sufficiently utilized. Discussion on these effects given below is based on authors' experimental results.

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RESULTS AND DISCUSSION

Activity increase effect

It is well-known that for catalytic organic and/or polymer synthesis the activity of the catalyst used is often the key factor which determines whether or not the synthesis could be successful. It has frequently observed in practical research and reported in references that immobilizing some a homogeneous metal complex catalyst on a polymer support will cause distinctly decrease of the complex's catalytic activity. According to our experience and long-term investigation this is definitely not unavoidable if only we tailor the structure of polymer support (chemical structure, physical structures: pore diameter, crosslinking density, specific areas etc.) carefully. For example, the heteronuclear metal cluster complex $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ is a highly active catalyst for the hydroformylation of 1-hexene. When it was immobilized on a tailor-made crosslinked polymaleic anhydride (PMA_n)—copolymer of maleic anhydride, styrene and divinyl benzene—the synthesized polymeric catalyst retained pretty well the homogeneous cluster complex's high catalytic activity (Table 1)^[5].

Table 1 Catalytic activity of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and its polymer supported counterpart for hydroformylation of 1-hexene^a

Catalyst	Conversion (%)	Specific activity ^b ($\text{kg}\cdot\text{h}^{-1}\cdot\text{mol}^{-1}$)	Selectivity of aldehyde formation (%)
$\text{Co}_2\text{Rh}_2(\text{CO})_{12}$	96.4	1.93	100
$\text{Co}_2\text{Rh}_2(\text{CO})_{12}/\text{PMA}_n^c$	100	2.21	100

a. Reaction conditions: 80°C, $\text{H}_2/\text{CO}=1:1$ (molar ratio), $P=55\text{ kg/cm}^2$;

b. Specific activity=Weight (kg) of converted 1-hexene per molar catalyst per hour;

c. Crosslinking density: 10%, bead size: 200 mesh

The homogeneous catalyst $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ is very sensitive to oxygen and moisture. Trace amount of oxygen and water existed in the reaction system will cause its decomposition and so as to decrease dramatically its hydroformylation activity. The recovered catalyst showed no activity for the hydroformylation is an evidence. In contrast, the polymer supported cluster is more stable. After several times' recycle no distinct decrease in catalytic activity was observed^[6].

Metathesis of olefines is a project attracting chemists' great attention in recent years. The homogeneous catalytic systems of molybdenum and tungsten, such as $\text{Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]-\text{EtAlCl}_2$, $\text{WCl}_6-\text{SnBu}_4$, are conventionally used for metathesis reaction. In the metathesis of 1-hexene when the catalyst $\text{Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]$ was im-

mobilized on a tailor-made polystyrene support both the catalytic system's activity and yield of metathesis reaction increased distinctly^[7] (Table 2).

Table 2 Catalytic activity of homogeneous and polymer supported molybdenum catalytic system for metathesis of 1-hexene^a

Cat.	Conversion (%)	Specific activity ($\text{kg}\cdot\text{h}^{-1}\cdot\text{mol}^{-1}$)	Metathesis yield (%)
$\text{Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]-\text{EtAlCl}_2$	36.2	0.78	30.1
$\text{Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]/\text{PS}^b-\text{EtAlCl}_2$	42.9	0.93	37.1

a. Reaction conditions: 40°C, 7h; b. Crosslinking density of polystyrene support: 10%

The support effect of catalytic system $\text{WCl}_6-\text{SnBu}_4$ in metathesis of 1-heptene is more obvious. Using a tailor-made crosslinked polystyrene to support WCl_6 the catalytic activity increased by two-folds and the metathesis yield increased by fourfold^[8] (Table 3).

Table 3 Activity of homogeneous and polymer supported tungsten catalytic system for metathesis of 1-heptene^a

Cat.	Conversion (%)	Specific activity ($\text{kg}\cdot\text{h}^{-1}\cdot\text{mol}^{-1}$)	Metathesis yield (%)
$\text{WCl}_6-\text{Bu}_4\text{Sn}$	27.4	2.69	14.5
$\text{WCl}_6/\text{PS}^b-\text{Bu}_4\text{Sn}$	56.3	5.53	54.7

a. Reaction conditions: 40°C, 2h; b. Crosslinking density of polystyrene support: 8%

Study on the stability of above-mentioned homogeneous and polymer supported catalytic systems for metathesis demonstrated that immobilizing increased the catalysts' stability dramatically and is responsible for the increase of activity of polymer supported catalytic system^[7].

Selectivity promotion effect

The selective hydrogenation of polyunsaturated organic compounds is a subject of both great theoretical and practical significance. The ruthenium complex $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ is a highly active and selective catalyst for selective hydrogenation of cyclododecatriene (CDT). The disadvantages of this catalyst are: (i) as a homogeneous catalyst after hydrogenation its separation with the reactant and product is a laborious task; (ii) as ruthenium is a noble metal so the decomposition and loss of the catalyst will cause great increase of production cost of the hydrogenation product. Unfortunately, in the practical production this decomposition and loss are actually unavoidable. In order to overcome these disadvantages we synthesized a polymer supported ruthenium complex catalyst by using a tailor-made crosslinked macroporous polystyrene as the support. Experimental results are listed in Table

4. It is very clear, from Table 4, that the polymer supported ruthenium complex not only retained the homogeneous complex's high activity and at the same time increased slightly the cyclododecene (CDE) formation selectivity of the hydrogenation reaction^[9,10].

Table 4 Hydrogenation properties of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ and the corresponding polymer supported catalyst^a

Catalyst	Conversion of CDT (%)	Selectivity for CDE (%)
$\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$	97	82
$[-\text{Ph}-\text{CH}_2-\text{P}(\text{Ph})_2\text{Ru}(\text{PPh}_3)_2\text{Cl}]^b$	93	84

a. Reaction conditions: 140°C, 40kg/cm², 2.5h; b. Support: polystyrene, crosslinking density 10%, average pore diameter: 20nm, bead diameter: 0.2~0.4mm

The better selectivity of polymer supported catalyst arises from the sieve effect of the tailor-made support. As in the case of either the average pore diameter of the support is greater or less than 20nm the selectivity of the polymer supported catalyst will decrease^[9].

The selectivity promotion effect of polymer supports can be seen more clearly in the case of metathesis of 1-hexene or 1-heptene catalyzed by polymer supported tungsten and molybdenum catalysts^[7,8]. Comparing to the homogeneous catalyst (No 1) the polymer supported tungsten catalyst (No 2) increased the selectivity of metathesis by more than two-fold (Table 5). At the same time the side reaction— isomerization of 1-hexene was reduced.

Table 5 Selectivity of homogeneous and the corresponding polymer supported tungsten, molybdenum catalysts for metathesis 1-hexene^a

No.	Catalyst	Conversion of 1-hexene (%)	Metathesis selectivity (%)	Isomerization of 1-hexene (%)
1	$\text{WCl}_6-\text{Bu}_4\text{Sn}$	25.5	41.2	6.1
2	$\text{WCl}_6/\text{PS}^b-\text{Bu}_4\text{Sn}$	43.1	97.4	5.8
3	$\text{Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]-\text{EtAlCl}_2$	36.2	83.1	15.0
4	$\text{Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]/\text{PS}^b-\text{EtAlCl}_2$	42.9	86.5	1.1

a. Reaction conditions: 40°C, 7h; b. Crosslinking density of the support: 10%.

Protection effect for labile species

In recent years research on ring opening metathesis polymerization (ROMP) of cycloolefines has attracted great attention in polymer chemistry circle owing to the outstanding achievements of this polymerization method in tailoring polymers' molecular structures and synthesizing new polymeric materials with excellent properties^[18]. ROMP of dicyclopentadiene (DCPD) catalyzed by catalytic systems

$(\text{ArO})_x\text{WCl}_{6-x}\text{Et}_y\text{AlCl}_{3-y}$ ($x = 1 \sim 4$, $y = 1$ or 2) gives a crosslinked polymer possessing excellent mechanical properties^[11]. We carried out ROMP of DCPD and found that when the homogeneous catalysts WCl_6 , $(\text{ArO})_3\text{WCl}_3$ (ArO : 2, 6-ditertiarybutyl-*p*-cresoxy) were immobilized on a tailor-made polystyrene not only the conversion of monomer, that is the activity of catalytic systems, was increased (Table 6), but also the mechanical properties of synthesized polydicyclopentadiene (PDCPD) were greatly improved (Table 7)^[11,12,17].

Table 6 Influence of immobilization of homogeneous catalysts on ROMP of DCPD

No	Catalyst	Gelation time (s)	Conversion of DCPD (%)
1	$\text{WCl}_6\text{—Et}_2\text{AlCl}$	65	94.6
2	$\text{WCl}_6/\text{PS—Et}_2\text{AlCl}$	55	97.7
3	$(\text{ArO})_3\text{WCl}_3\text{—Et}_2\text{AlCl}_2$	78	97.9
4	$(\text{ArO})_3\text{WCl}_3/\text{PS—Et}_2\text{AlCl}_2$	72	97.9

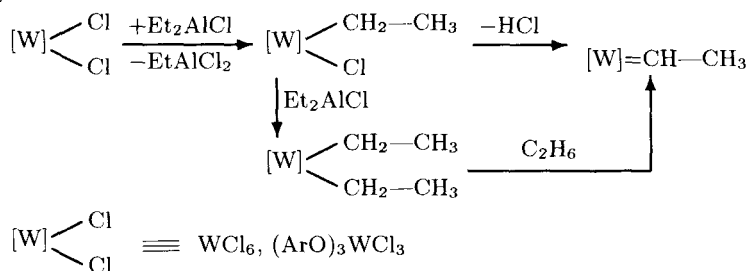
Reaction conditions: 80°C , DCPD: Cat.= 10^4 (molar ratio)

Table 7 Influence of immobilization of homogeneous catalysts on the mechanical properties of PDCPD synthesized by ROMP

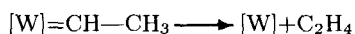
No	NIS (kg·cm/cm)	TS (MPa)	FS (MPa)	BER (%)
1	36.4	32.8	47.4	1.5×10^2
2	47.6	40.0	47.7	1.3×10^2
3	38.3	38.5	68.0	1.4×10^2
4	52.4	44.4	71.0	1.4×10^2

NIS: notched impact strength (measured by Izod impact tester); TS: tensile strength; FS: flexural strength, BER: breaking elongation ratio

According to a well-accepted viewpoint, the really catalytic active species initiating the ROMP is a metallocarbene species, that is a tungstennocarbene in this case, generated as follows:



In the case of homogeneous catalysis the metallocarbene species, an extremely labile species, decomposes very easily^[7,11]:



Study on the ageing of homogeneous and polymer supported catalysts for metathesis reaction of olefins, which has catalytic active species of same nature as in ROMP of cycloolefins, demonstrated that in the presence of polymer supports the metal-carbene species is far more stable than it is in the case of homogeneous catalysis^[7,8]. Our on-going experiments on ageing of catalytic systems for ROMP reveal the same internal factor. The increase of stability of catalytic species is favoured for the thoroughly proceeding of crosslinking polymerization and as a result not only the monomer conversion of the polymerization increased which is due to more unpolymerized DCPD molecules can reach the propagating macromolecular metallocarbene active centers, at the same time the mechanical properties of synthesized PDCPD are dramatically improved which are probably due to the increase of crosslinking density of PDCP.

The presence of polymer supports prevents the colloidal metal particles from aggregation and is an additional evidence on protection effect of polymer supports for labile species. For example, colloidal palladium alone can not be used as a hydrogenation catalyst as it tends to aggregate, as a result its catalytic hydrogenation activity is very poor. Using it as a catalyst for hydrogenation of cyclododecatriene (CDT) the conversion is only 6.2% (Table 8).

Table 8 Hydrogenation of CDT by polymer protected palladium catalysts

Catalyst	Conversion of CDT (%)	Selectivity (%)		
		CDD	CDE	CDA
Pd(collodal)	6.2	100	0	0
Pd/LPNVP	14.1	65.3	24.5	10.2
Pd/CPNVP	100	0	0	100

Reaction conditions: 100°C, 1.96MPa, 6h

When the colloidal palladium was supported on a linear poly-N-vinylpyrrolidone (LPNVP) the catalyst's hydrogenation activity increased by times. A tailor-made crosslinked poly-N-vinylpyrrolidone (CPNVP) supported colloidal palladium catalyst's hydrogenation activity increased by 16 times (Table 8). The X-ray diffraction analysis and scanning electron microscopic analysis of CPNVP supported catalyst indicated that palladium particles are evenly distributed on the support taking the particle size of colloid (4.2 nm). The presence of polymer supports effectively prevents the colloidal palladium particles from aggregation. It is a strong evidence that the polymer supported catalyst Pd/CPNVP was recycled for 20 times and during this course both the catalyst's hydrogenation activity and the particle size of colloidal palladium on the support did not show any substantial changes^[13].

Reusability increase effect

In a lot of cases the reusability of homogenous metal complex catalysts is poor. Some of them even can be used for only one time and when being reused not only the catalytic activity decreases sharply, the structure of the complex may also have changed substantially. In our experience, when the homogeneous catalysts were immobilized on tailor-made polymer supports the reusability of the synthesized catalysts may increase by ten-fold or more. For example, as a catalyst for the selective hydrogenation of CDT the polymer supported ruthenium complex $[-\text{Ph}-\text{CH}_2-\text{P}(\text{Ph})_2-\text{Ru}(\text{PPh}_3)_2\text{Cl}_2]$ was recycled for 20 times without any substantial changes in the activity and selectivity^[10]. Similar circumstances were observed for polymer supported palladium hydrogenation catalysts^[9,13,14], and for polymer supported rhodium complex catalysts for hydroformylation^[15,16].

CONCLUSION

The polymer support effects of metal complexes—immobilizing homogeneous metal complexes on polymers increases the complexes' catalytic activity, selectivity, reusability and stability of labile catalytic species etc—are observed from time to time in polymer-mediated organic and polymer synthesis. A key factor for making good use of these effects is to tailor the polymer supports carefully and systematically. Though this is a time-consuming and complicated work, however, it has proved itself effective. According to our experience the catalytic behaviour of polymer supported metal complexes is often unsatisfactory in the case of using commercially available resins as supports.

REFERENCES

- [1] Merrifield, R.B., *J. Am. Chem. Soc.*, **1963**, *85*, 2149
- [2] Abbott, B.J., *Adv. Appl. Microbiol.*, **1976**, *20*, 203
- [3] Grubbs, R.H., Gibbons, G., Kroll, L.C., Bonds, Jr.W.D., Brubaker, Jr.C.H., *J. Am. Chem. Soc.*, **1973**, *95*, 2373
- [4] Davankov, V.A., Zolotarev, Y.A., *J. Chromatogr.*, **1978**, *155*, 285
- [5] He, B.L., Sun, J.T., Li, H., Sang, J.J., *Ion Exch. and Adsorp. (Chin.)*, **1989**, *5* (6), 420
- [6] He, B.L., Sun, J.T., Li, H., Sang, J.J., *J. Macromol. Sci. -Chem.*, **1989**, *A26* (2 & 3), 417
- [7] Liao, S.J., Guo, Y.P., Yu, S.W., Yu, D.R., Guo, H.F., He, B.L., Sun, J.T., Li, H., *Chin. J. Mol. Catal.*, (Selected papers), **1989**, (1), 35

- [8] Yao, J.S., Li, H., Sun, J.T., He, B.L., *Chin. J. React. Polym.*, **1994**, 3 (1~2), 8
- [9] Li, H., He, B.L., *React. and Func. Polym.*, **1995**, 25, 61
- [10] Zhao, W.J., Li, H., Zhang, S.J., Fang, Y.Q., Sun, J.T., He, B.L., *Petrochem. Tech. (Chin.)*, **1984**, 13, 582
- [11] Li, H., Wang, Z., Wang, Y.Q., He, B.L., *React. and Func. Polym.*, **1997**, 33, 193
- [12] Li, H., Wang, Z., He, B.L., *Ion Exch. and Adsorp. (Chin.)*, **1997**, 13 (3), 302
- [13] He, B.L., Sun, J.T., Li, H., Jin, X.N., *Chem. J. Chin. Univ. (Chin.)*, **1990**, 11 (5), 521
- [14] Chen, C.F., Sun, J.T., Li, H., He, B.L., *Chin. J. Polym. Sci. (Engl. ed.)*, **1990**, 8 (4), 295
- [15] He, B.L., Sun, J.T., Li, H., Sang, J.J., *Chin. J. Polym. Sci. (Engl. ed.)*, **1990**, 8 (2), 158
- [16] He, B.L., Sun, J.T., Li, H., Zheng, F.P., Cai, H.Q., *Scientia Sinica, B*, **1987**, 30 (1), 16
- [17] Li, H., *Abstracts of Chinese Academic Journal*, **1996**, 2 (9), 109
- [18] Li, H., Wang, Z., Jin, X.B., He, B.L., *Ion Exch. and Adsorp. (Chin.)*, **1997**, 13 (2), 216