

Surface active rhodium catalysts for hydroformylation of higher alkenes in two-phase systems

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Abstract

A variety of water-soluble phosphine and phosphite ligands with phase-transfer ability based on functionalized polyethylene oxide has been synthesized. The corresponding rhodium complexes show high catalytic activity in aqueous biphasic hydroformylation of higher alkenes under mild conditions. The catalysts can be easily separated from products and reused. The effect of ligands structure, temperature, ligand-to-rhodium ratio, addition of free PPh_3 and P(OPh)_3 on catalytic stability and activity is studied. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of water-soluble transition metal complexes as catalysts for various reactions, e.g., hydrogenation, hydroformylation and carbonylation has recently received much attention [1].

Aqueous catalysis is of considerable academic and industrial interest because water is a more environmentally compatible solvent and because water-soluble catalysts can be easily separated from organic products [2].

The combination of transition metal catalysis and phase transfer catalysis can be employed in

a wide range of organic reactions and gives a number advantages since this approach makes it possible to use more available substances and aqueous solutions instead of expensive and often dangerous reagents and solvents that should be thoroughly dried.

The most commonly used catalysts for hydroformylation in water–organic solvent media are various sulfonated and carboxylated phosphines [3]. Addition of phase transfer agents into a reaction medium considerably increases the reaction rate and the selectivity with respect to the target products, and variation of the nature of a surfactant allows one to readily attain fast phase separation.

It is also reported that various surface-active phosphines can be used as ligands in catalytic complexes, and the reaction rate linearly in-

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creases with increasing length of the alkyl chain of a ligand [4–6].

We assumed that water-soluble surface-active ethylene oxide oligomers, which can be easily functionalized at a terminal hydroxyl group, can be employed for controlled synthesis of metal complexes that combine the properties of both a catalyst and a phase transfer agent within the same molecule. Monobutyl ether of polyethylene oxide REOH, where $R = \text{BuO}$, and $E = (\text{CH}_2\text{CH}_2\text{O})_{111}\text{CH}_2\text{CH}_2-$, with the molecular weight 5000 was chosen to produce ligands.

2. Experimental

Polymer ligands REPh_2 , REOPPh_2 , and $(\text{REO})_2\text{PPh}$, REOP(OPh)_2 were synthesized according to the indicated literature procedures [7,8].

The content of modifying groups was calculated from ^1H NMR spectra with hexamethylenedisiloxane as an internal standard and was 0.3–0.7 mmol per 1 g of polymer for all types of ligands. ^{31}P NMR spectra exhibit signals typical for the corresponding compounds.

Functionalized oligomers were subjected to ligand exchange with rhodium(I) dicarbonyl acetylacetonate $[\text{Rh}(\text{acac})(\text{CO})_2]$ in an argon atmosphere.

IR spectroscopy and elemental analysis suggest that the oligomer complexes produced have the formula $\text{Rh}(\text{acac})[\text{L}]_2$. IR spectra of the complexes exhibit intense absorption bands of coordinated ligands: acetylacetonate (1606 and 1593 cm^{-1}) and polymer ones (Table 1). No bands of stretching vibrations of coordinated CO-ligands (2070 and 2010 cm^{-1}) occur in the spectra (Table 1).

The catalysts produced thus were tested in model reaction of 1-dodecene hydroformylation in the two-phase water–organic system. Polymer chain of a ligand plays the role of a surfactant. The reaction was performed in a controlled-temperature steel autoclave 30 ml in vol-

Table 1
Rhodium macrocomplexes

Complex	Rhodium content, wt. %		$\nu_{\text{L-Rh}}$, cm^{-1}
	Calc.	Found	
$[\text{REPh}_2]_2\text{Rh}(\text{acac})$	0.98	0.89	1519, 1438
$[\text{REOPPh}_2]_2\text{Rh}(\text{acac})$	0.98	0.94	1471, 1459
$[(\text{REO})_2\text{PPh}_2]_2\text{Rh}(\text{acac})$	0.45	0.38	1473, 1463
$[\text{REOP(OPh)}_2]_2\text{Rh}(\text{acac})$	0.98	0.91	1227, 985

$R = \text{C}_4\text{H}_9\text{O}-$; $E = (\text{CH}_2\text{CH}_2\text{O})_{111}\text{CH}_2\text{CH}_2-$.

ume with a magnetic stirrer at a pressure of synthesis gas of 0.1–1.5 MPa, the carbon dioxide-to-hydrogen ratio 1:1, and temperatures from 20 to 95°C. A reaction mixture contained 0.0024 g (0.0093 mmol) of $\text{Rh}(\text{acac})(\text{CO})_2$, the corresponding amount of polymer ligand, 1.5 ml of toluene, 1.34 mmol of olefin, and 1.5 mol of water. The aqueous layer containing a metal complex was separated, and a reaction mixture was analyzed by CG on a Chrom-5 gas chromatograph and CG-MS using a Finnigan-MAT-1125 CG-MS system. If hydroformylation was carried out in the absence of water, the organic solvent amount was increased to 3.0 ml.

^1H and ^{31}P NMR analyses were conducted with a Varian XL-300 spectrometer.

FTIR spectra of polymer samples produced as KBr-containing pellets were recorded with a Perkin Elmer 2000 Fourier-transform spectrometer in the range 550–3500 cm^{-1} .

3. Results and discussion

Electron-donor properties of a ligand in a catalyzing complex are known to considerably affect peculiarities and conditions of reactions between olefins and synthesis gas. Therefore, we considered it interesting to study the possibility to perform hydroformylation with the use of rhodium-containing catalysts based on polyethylene oxides modified by phosphorus-containing terminal groups with various electron densities at the phosphorus atom.

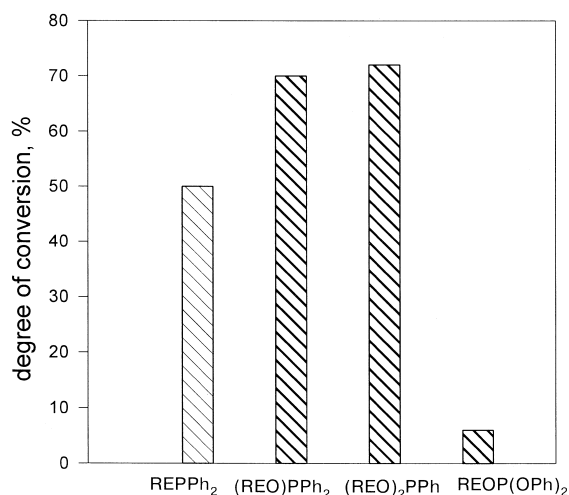


Fig. 1. Effect of ligand structure on catalytic activity in hydroformylation of dodecene-1 in the toluene/water [reaction time 6 h; $T = 50^{\circ}\text{C}$; synthesis-gas pressure 1.5 MPa].

We synthesized a number of ligands with sequentially increasing electron-acceptor power: REPPh₂, REOPPh₂, (REO)₂PPh and REOP(OPh)₂.

The main products of 1-dodecene hydroformylation were tridecanal and 2-methyldodecanal. In all cases, the products of hydrogenation and isomerization of the double bond were observed to form with the yield not more than 3–5%.

Degree of conversion of olefines to aldehydes after 6 h of reaction was used as a param-

eter estimating the activity and the selectivity of the catalysts under investigation. In the two-phase system (water/organic solvent, olefine) quantitative conversion was achieved within 10–16 h.

Catalytic systems based on three of the four ligands studied, specifically, REPPh₂ [L1], REOPPh₂ [L2] and (REO)₂PPh [L3] (Fig. 1), exhibited a high catalytic activity. The catalytic activities of these ligands in hydroformylation increase in the order



The results presented show that an increase in the number of phosphite bonds in a ligand and, hence, in the electron affinity of a complex-forming site, causes the increase in the catalytic activity of the complex based on this ligand. However, when triphosphite REOP(OPh)₂ [L4] was used as a ligand, the degree of conversion of the initial olefin was only 6%. We consider that such a low activity of this catalytic complex can be related to the hydrolysis of polymer phosphite, since triphosphites are very sensitive to the presence of water. Ligands L2 and L3 can also be expected to be partially hydrolyzed; however, these phosphine–phosphites turned out to be quite stable and did not lose their activity for five catalyst cycles. We relate such a high hydrolytic stability to the presence of a polymer

Table 2
Effect of ligand–rhodium ratio on stability of catalysts in recycling experiments

Entry	L:Rh ratio	Degree of conversion into aldehydes, %			<i>n/i</i> Ratio		
		L1	L2	L3	L1	L2	L3
1	4	5	15	20	1.7	1.8	2.0
	reuse	3	7	12	1.7	1.8	2.0
2	6	10	25	46	1.7	1.9	2.1
	reuse	7	15	32	1.7	1.9	2.1
3	10	38	48	55	1.8	2.0	2.0
	reuse	25	38	42	1.8	2.0	2.0
4	15	45	68	70	1.9	2.1	2.0
	reuse	43	65	68	1.9	2.1	2.0
5	20	35	50	62	1.9	2.1	2.0
	reuse	33	49	61	1.9	2.1	2.0
6	30	8	45	58	2.0	2.1	2.0
	reuse	7	45	58	2.0	2.1	2.0

Reaction time 6 h; $T = 50^{\circ}\text{C}$; synthesis-gas pressure 1.5 MPa.

chain in the phosphite fragment of a ligand, since the size of a radical contained in a phosphite is known to have a determining effect on its hydrolysis [9].

It has been known that one of the causes for deactivation of rhodium-containing catalysts with phosphorus-containing ligands in hydroformylation is the formation of less active complexes $[\text{Rh}(\text{CO})\text{L}_2]_2$ and completely inactive orthometallated compounds and a bridging phosphide ligand [10,11]. It is possible to avoid formation of such inactive in hydroformylation particles and, hence, to increase the degree of conversion by adding excess of free ligand into a reaction medium. Therefore, we studied the effect of content of both free polymer ligand

and low-molecular phosphine PPh_3 in a reaction mixture on hydroformylation. Tables 2 and 3 present the results.

The optimum ligand-to-rhodium ratio L:Rh, which ensured the maximum degree of conversion, was found to be 15:1 for all catalytic systems. In addition, a catalyst with this L:Rh ratio did not lose its activity in reuse.

An increase in the polymer ligand content in a reaction mixture caused a loss of stability of a catalytic complex, which was indicated by the decrease in the degree of dodecene conversion in reuse of the same catalyst charge. A further increase in the L:Rh ratio above 15:1 noticeably retarded hydroformylation (the degree of conversion of the initial reactant after 6 h of reac-

Table 3

Effect of addition of PPh_3 into catalytic system in hydroformylation of 1-dodecene in the hexane/water

Entry	Ligand	Rh:L ratio	Rh: PPh_3 ratio	Degree of conversion into aldehydes, %	n/i ratio	Note
1	REPPH ₂	1:2	1:3	83	3.5	}
2		1:2	1:3	30	3.5	
3		1:2	1:6	90	3.6	
4		1:2	1:15	40	5.3	
5		1:2	1:30	17	7.5	}
6		1:15	1:3	90	3.6	
7		1:15	1:3	82	3.6	
8		1:15	1:3	77	3.6	
9	REOPPH ₂	1:2	1:3	85	3.6	}
10		1:2	1:3	17	3.6	
11		1:15	1:3	83	3.4	}
12		1:15	1:3	80	3.4	
13		1:15	1:3	78	3.3	
14	(REO) ₂ PPH	1:2	1:3	90	4.0	}
15		1:2	1:3	30	3.8	
16		1:15	1:3	90	4.0	}
17		1:15	1:3	87	4.0	
18		1:15	1:3	85	4.0	

Catalysts system $\text{Rh}(\text{acac})[\text{L}]_2 + \text{PPh}_3$; reaction time 6 h; $T = 50^\circ\text{C}$; synthesis-gas pressure 1.5 MPa.

* Experiments were carried out with a single catalyst charge.

tion decreased). In our opinion, this is brought about by the hindrance to olefin coordination with the rhodium atom that emerged in large excess of free ligand.

A similar pattern was also observed for catalytic systems containing excess of triphenylphosphine. An increase in the triphenylphosphine-to-rhodium ratio $\text{PPh}_3:\text{Rh}$ to 6:1 had favourable effect on catalytic activity, but a further increase in the low-molecular phosphine concentration perceptibly decreased the reaction rate.

The ratio between the yields of normal and branched aldehydes was independent of the polymer ligand concentration in a reaction mixture. At the same time, triphenylphosphine addition to $\text{PPh}_3:\text{Rh} = 30:1$ increased the selectivity with respect to tridecanal to 7.5. However, as has been already noted, this caused the decrease in the efficiency of catalytic systems: the degree of dodecene conversion after 6 h of reaction attained only 17%. We assumed that the structure of catalyzing complexes remains unchanged in hydroformylation. This was indicated by the virtually constant degree of conversion of the initial olefin in the same time interval in multiple reuse of the same catalyst charge, and the data of elemental analysis and IR spectroscopy. For example, the losses of rhodium after five catalyst cycles were only 0.02% of its initial content, and IR spectrum remains the same.

The temperature dependence of the tridecanal and 2-methyldodecanal yields was studied by the example of hydroformylation in the presence of the catalytic system $\text{Rh}(\text{acac})[\text{L}3]_2$ (Fig. 2). The activity was highest at 50°C. At this temperature, the conformation of the polymer chain of a ligand was probably attained such that the metal site was most accessible to ensure emergence of the active catalyst form.

Toluene, hexane, and diethyl ether were used as organic solvents in 1-dodecene hydroformylation in a two-phase system.

As Table 4 shows, organic solvent does not substantially affect the degree of conversion of

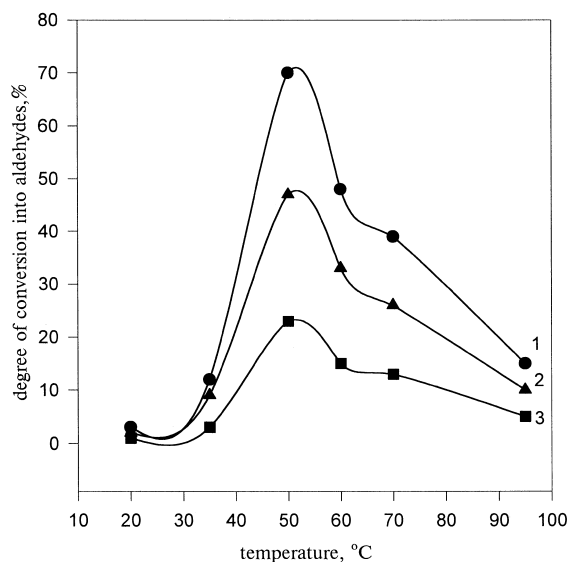


Fig. 2. Temperature dependences of the yields of aldehydes (1), tridecanal (2), and 2-methyldodecanal (3) 1-dodecene hydroformylation in the toluene/water.

the initial olefin and the selectivity with respect to linear aldehyde. However, the use of ether or hexane as an organic phase opens up possibility for multiple reuse of the same catalyst charge without considerable loss of activity. We demonstrated that the macrocomplex-containing aqueous phase can be multiply reemployed in reaction: the degree of conversion of the initial reactant was virtually unchanged after five hydroformylation cycles (Table 4). When toluene was used, an attempt to repeat reaction with synthesis gas resulted in that the yields of aldehydes were almost halved in even the second hydroformylation cycle. This is probably related to the fact that the polymer catalyst partially dissolved in the toluene to cause a decrease in its content in the aqueous phase.

We also found that the macrocomplex synthesized allows one to perform hydroformylation in the absence of organic solvent in the olefin–water system. The high reactant-to-catalyst ratio obtained (to 725:1) considerably increases the efficiency of the metal complex.

We also showed that 1-dodecene hydroformylation catalysts based on ethylene glycol

Table 4
Hydroformylation of 1-dodecene in the water/organic solvent system

Organic solvent	Degree of conversion into aldehydes, %			<i>n/i</i> Ratio		
	L1	L2	L3	L1	L2	L3
Toluene ^a	43	65	70	1.9	2.0	2.0
	20	25	40	1.8	2.1	2.0
Ether	40	63	60	1.8	2.0	2.2
Hexane ^a	45	68	70	1.8	2.1	2.0
	43	65	70	1.8	1.9	2.1
	40	60	68	1.9	2.0	2.0
	40	60	65	1.8	2.0	2.0
Without solvent ^a	35	60	65	1.7	2.0	2.0
	38	55	65	1.7	2.0	2.1
	35	52	63	1.7	2.0	2.0
	30	48	60	1.7	1.9	2.0

Reaction time 6 h; *T* = 50°C; synthesis-gas pressure 1.5 MPa.

^aExperiments were carried out with a single catalyst charge.

oligomers functionalized by phosphine and phosphite groups can be successfully used not only in phase-transfer catalysis but also in a homogeneous medium (Table 5).

In the latter case, if anhydrous ether was added into a reaction mixture after reaction completion, catalyst completely precipitated, and could be readily separated from the reaction products and reused without considerable loss of its activity. No changes occurred in the structure of a metal complex as determined by elemental analysis and IR spectroscopy.

The fact that the activity of catalysts with phosphite ligands is higher than that of catalysts

with phosphine ligands was noted in many works. Therefore, in our opinion, of special interest was the catalytic system Rh(acac)[L4]₂, which exhibited a high catalytic activity at a synthesis-gas pressure of even 0.2 MPa (the degree of conversion after 6 h of reaction was 65%).

By the example of this complex, we studied the dependences of the basic characteristics of 1-dodecene hydroformylation in toluene on time, temperature, synthesis-gas pressure, and L:Rh ratio in the catalytic system.

Fig. 3 shows that much of the initial olefin (94%) transformed into aldehydes in 6 h, and

Table 5
Homogeneous 1-dodecene hydroformylation

Entry	Ligand	L:Rh ratio	Aldehyde content, %		Degree of 1-dodecene conversion, %
			Tridecanal	2-Methyldodecanal	
1	(L1)	15	51	25	79
	reuse	15	47	23	73
2	(L2)	15	52	23	77
	reuse	15	47	21	72
3	(L3)	15	54	21	77
	reuse	15	50	20	75
4	(L4) ^a	10	55	11	68
	reuse ^a	10	50	10	63

Reaction time 6 h; *T* = 50°C; synthesis-gas pressure 1.5 MPa; solvent toluene.

^aExperiment was carried out at a pressure of 0.2 MPa.

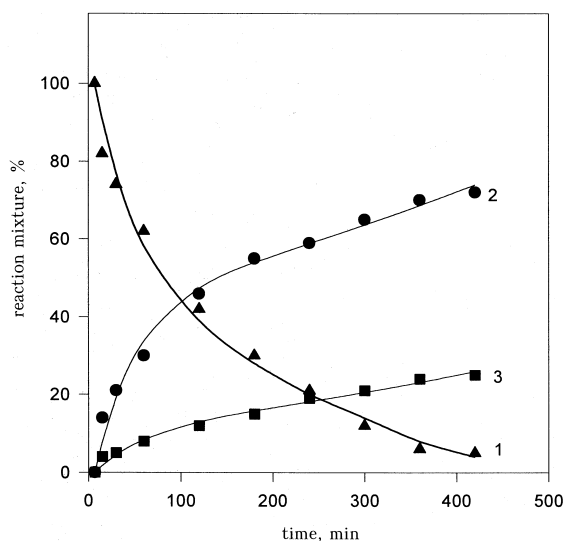


Fig. 3. Variation of reaction time in the hydroformylation of dodecene-1: (1) 1-dodecene, (2) tridecanal, and (3) 2-methyl-dodecanal. [Catalyst $\text{Rh}(\text{acac})[\text{REOP}(\text{OPh})_2]_2$; 50°C , L:Rh = 4:1, synthesis-gas pressure 0.2 MPa, solvent toluene].

the ratio between the tridecanal and 2-methyl-dodecanal yields was virtually time-constant.

As in reaction in a two-phase system the optimum temperature was 50°C . Its further increase caused the decrease in aldehyde yield.

With increasing the synthesis-gas pressure, the degree of reactant conversion linearly increased, and the yield became quantitative at the pressure 0.3 MPa.

Olefin hydroformylation with catalysts containing phosphite ligands was performed in excess of free ligand, which was assumed [12] to inhibit formation of inactive complexes such as $\text{Rh}_4(\text{CO})_8\text{L}_4$. In addition, an increase in the free ligand content in a reaction mixture favored an increase in the reaction selectivity with respect to n -aldehyde by occupying the rhodium coordination sphere and, thus, creating conditions for preferable formation of linear acyl intermediates. For various catalytic systems, the optimum metal-to-ligand ratio was chosen individually and depended on both electron and steric properties of ligand.

Table 6 shows that an increase in the L:Rh ratio caused an increase in the selectivity with

Table 6
Homogeneous 1-dodecene hydroformylation at various ligand/rhodium ratios

L:Rh ratio	Degree of conversion into aldehydes, %	n/i Ratio
2	38	2.2
3	88	2.4
4 ^a	94	3.5
4 ^a	51	3.2
6	72	3.0
10 ^a	61	5.0
10 ^a	54	5.0
10 ^a	53	4.9

Catalyst $\text{Rh}(\text{acac})[\text{REOP}(\text{OPh})_2]_2$; reaction time 6 h; $T = 50^\circ\text{C}$; synthesis-gas pressure 0.2 MPa, solvent toluene.

^aExperiments were carried out with a single catalyst charge.

respect to tridecanal from 2.2 at the stoichiometric ratio L:Rh = 2 to 5.0 in 10-fold excess of ligand. In addition, the stability of the oligomer catalyst increased. For example, a catalyst that did not contain free (polyethylene oxide)diphenylphosphite could not be reused. The degree of conversion in reusing a complex with the L:Rh ratio 4:1 was almost halved, whereas a catalyst with the L:Rh ratio 10:1 virtually did not lose its activity in triple reuse. In the latter case, however, the degree of conversion was considerably lower. This can be related to the inhibition of dissociation of the initial metal complex, which is a necessary step in formation of catalytically active particles.

Table 7 demonstrates the effect of adding low-molecular phosphite. An addition of four-

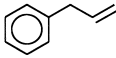
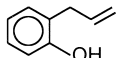
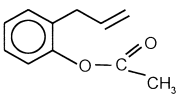
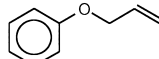
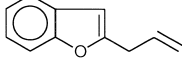
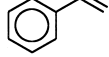
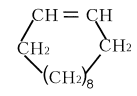
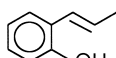
Table 7
1-Dodecene hydroformylation in the presence of triphenylphosphite

$\text{P}(\text{OPh})_3$:Rh ratio	Degree of 1-dodecene conversion, %	n/i Ratio
4 ^a	85	7.7
4 ^a	79	7.5
8	77	7.9
12	61	7.6
16	45	5.4

Catalyst $\text{Rh}(\text{acac})[\text{REOP}(\text{OPh})_2]_2$; $\text{REOP}(\text{OPh})_2$:Rh = 2:1; reaction time 6 h; $T = 50^\circ\text{C}$; synthesis-gas pressure 0.2 MPa, $(\text{CO}/\text{H}_2 = 1/1)$.

^aExperiments were carried out with a single catalyst charge.

Table 8
Hydroformylation of olefins

Ligand, conditions	(REO) ₂ PPh; toluene/water, 1.5MPa, 50 °C		REOP(OPh) ₂ ; toluene, 0.2MPa, 50 °C	
	Degree of conversion into aldehydes, %	n/i ratio	Degree of conversion into aldehydes, %	n/i ratio
	87	1.3	92	9.5
	72	1.0	51	1.7
	96	0.8	90	1.7
	68	1.6	54	0.8
	78	0.5	74	1.1
	88	1.0	78	0.5
	no reaction	---	37*	---
	no reaction	---	45*	---

* Pressure 1.5 MPa.

fold (in terms of metal content) excess of P(OPh)₃ brought about an abrupt increase in the normal-aldehyde yield. A further increase in the low-molecular ligand concentration in a reaction medium did not increase in the *n/i* ratio but substantially decreases the reaction rate. The latter is probably caused by the hindrance to reactant coordination at the rhodium atom in the presence of large excess of readily coordinating triphenylphosphite.

In reaction with low-molecular phosphite, a catalyst can also be separated completely from the reaction products and reused.

In conclusion we have demonstrated that the use of macromolecular catalysts can be ex-

tended to a variety of other water-insoluble olefins containing an aromatic and heterocyclic fragment (Table 8). All the substrates investigated readily enter in to the reaction, and the main product are the corresponding aldehydes.

4. Conclusion

The results obtained suggest that the polymer catalysts proposed are active in olefins hydroformylation under mild conditions in both the two-phase water–organic solvent system and a homogeneous medium. In addition, these catalysts can be multiply reused without additional

regeneration and without loss of their catalytic activity.

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