

## Polymeric rhodium-containing catalysts in olefin hydroformylation

*E. V. Slivinskii*<sup>†</sup> and *N. V. Kolesnichenko*<sup>\*</sup>

*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,  
29 Leninsky prosp., 119991 Moscow, Russian Federation.  
Fax: +7 (095) 485 0922. E-mail: nvk@ips.ac.ru*

The main results obtained by studying hydroformylation of olefins on polymeric rhodium-containing catalysts are reviewed. Different types of N-containing polymeric ligands capable of hydroformylating under conditions of heterogeneous catalysis are considered. Possibilities of using water-soluble polymers containing quaternary ammonium groups are shown. The data on the influence of a polymeric matrix on the catalytic properties of the rhodium catalyst of olefin hydroformylation are presented.

**Key words:** hydroformylation, olefins, water-soluble rhodium complexes, N-containing polymers, polyelectrolytes.

Carbonylation processes are to date the most promising, energetically saving, and ecologically pure methods for functionalization of unsaturated compounds.<sup>1,2</sup> Industrial hydroformylation of olefins on rhodium catalysts makes it possible to increase the efficiency of the process and involve oxo synthesis technologies in the production of valuable petrochemical products and intermediates. However, hydroformylation is put into use more slowly than its potentialities offer. The reason, probably, lies in the problem of separation of catalyst from reaction products upon the hydroformylation of medium- and high-molecular olefins.

Rhodium catalysts can widely be used only in highly stable and technologically reasonable catalytic systems, in particular, as heterogenized catalysts that combine a high activity, simple separability from reaction products, and a long catalyst life without additional regeneration.<sup>3,4</sup>

Nitrogen-containing polymers that provide stable rhodium fixation and easy catalyst separation from reaction products seem to be promising.

In this work, we present the results on the development of basically new highly efficient catalytic systems based on the rhodium complexes and N-containing polymers for hydroformylation of medium-molecular olefins under phase transfer and heterogeneous conditions. The structures and properties of the polymers under study are presented in Table 1.

The following compounds were chosen as the main objects of the study: hex-1-ene, whose hydroformylation is a promising method for synthesis of enantioaldehyde (intermediate product in syntheses of oximes, which are highly efficient extracting agents of nonferrous metals)

and isobutene along with but-2-enes which produce isovaleraldehyde and 2-methylbutanal, intermediate products in the syntheses of corvalolum and isoprene, respectively.

Olefins were hydroformylated according to known procedures<sup>5,6</sup> in a stainless steel autoclave in a periodical regime with vigorous stirring at a constant pressure of 6 MPa (CO : H<sub>2</sub> = 1) and temperature 90 °C until virtually complete conversion of olefin was achieved.

A measure of catalyst activity was the hydroformylation rate determined as the number of moles of converted synthesis gas per time unit. Stability of the catalyst was estimated from the reaction rate by repeated testing of a catalyst after the reaction products were separated from the catalyst.

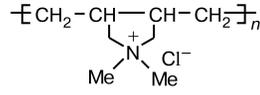
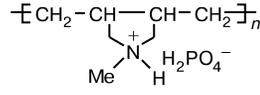
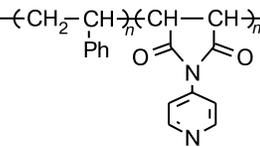
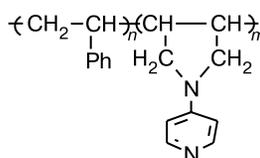
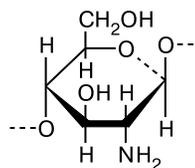
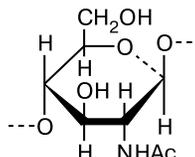
Reaction products were analyzed on a Chrom-5 chromatograph (capillary column 25 m long, phase poly(ethylene glycol)-20M, flame-ionization detector, carrier gas helium). Products of conversion of but-2-enes and isobutene were analyzed at 110 °C, and the temperature-programmed regime from 80 to 120 °C was used to analyze C<sub>7</sub> aldehydes.

In the case of isobutene hydroformylation, the single reaction product is isovaleraldehyde. When hex-1-ene reacts with H<sub>2</sub> and CO, the reaction mixture contains 2-methylhexanal and 2-ethylpentanal, while the reaction mixture obtained from hydroformylation of but-2-enes contains *n*-pentanal in addition to 2-methylbutanal. The selectivity with respect to the target product was determined in each case as the target product fraction in the total mixture of aldehydes.

The use of water-soluble N-containing polyelectrolytes as macroligands makes it possible to develop methods for controlling the catalytic properties of Rh-containing

<sup>†</sup> Deceased.

**Table 1.** Structures and molecular weights (M) of nitrogen-containing polymeric macroligands

Macroligand	Structure	M
PEI	$\text{-(CH}_2\text{-CH}_2\text{-NH)}_n\text{-}$	10000
WPC	$\text{-(CH}_2\text{-CH-CH-CH}_2\text{)}_n\text{-}$ 	30000
PHP	$\text{-(CH}_2\text{-CH-CH-CH}_2\text{)}_n\text{-}$ 	30000
STPM	$\text{-(CH}_2\text{-CH)}_n\text{-(CH-CH)}_m\text{-}$ 	70000
STPP	$\text{-(CH}_2\text{-CH)}_n\text{-(CH-CH)}_m\text{-}$ 	70000
Chitosan		60000
Chitin		60000

systems by optimizing the aqueous phase composition (pH change, introduction of additional low-molecular electrolytes, *etc.*).

Water-soluble macroligands were polyethyleneimine (PEI) and polycations (PC) of diallylic structure: water-soluble polycation (WPC) poly-*N,N*-diallyl-*N,N*-dimethylammonium chloride and poly-*N,N*-diallyl-*N*-methylaminodihydrophosphate (PHP).

The catalytic system based on  $\text{RhCl}_3$  and polyethyleneimine differs significantly from other systems (Table 2). Even after a prolong induction period (10–12 h), this system exhibits a very low activity in the hydroformylation of but-2-enes and hex-1-ene but a high selectivity with respect to 2-methylbutanal. Under identical conditions in the homogeneous catalytic hydroformylation of but-2-enes, selectivity with respect to 2-methylbutanal does not exceed 70–75%. The duration of the induction period and activity of the catalytic system are virtually indepen-

**Table 2.** Catalytic properties of the rhodium complexes with water-soluble macroligands in olefin hydroformylation

Olefin	Macroligand	Catalytic properties		
		$\tau/\text{h}$	$W \cdot 10^3$ /mol min <sup>-1</sup>	<i>S</i> (%)
But-2-ene	PEI	12	0.04	98*
	WPC	1	1	78*
	PHP	0.5	0.9	79*
Hex-1-ene	PEI	10	0.04	42**
	WPC	0	3.2	41**
	PHP	0	1.2	42**

*Note.* Conditions for olefin hydroformylation:  $T = 90^\circ\text{C}$ ,  $P = 6\text{ MPa}$  ( $\text{CO} : \text{H}_2 = 1$ ), reaction medium *p*-xylene–water,  $[\text{Rh}] = 8.7 \cdot 10^{-4}\text{ mol L}^{-1}$ ;  $\tau$  is the induction period;  $W$  is the reaction rate determined as the number of moles of the reacted synthesis gas per time unit;  $S$  is the selectivity of the reaction with respect to 2-methylbutanal (\*) or *n*-heptanal (\*\*).

dent of the structure of the polyethyleneimine ligand. A decrease in the molar ratio PEI/Rh reduces the induction period and insignificantly increases the hydroformylation rate.<sup>7</sup>

The catalysts based on the rhodium complexes with WPC and PHP have a high activity (close to the conventional activity in homogeneous hydroformylation) and a low selectivity with respect to 2-methylbutanal (78–79%) and *n*-heptanal (41–42%) characteristic of the unmodified rhodium complexes. All catalytic systems retain their properties after the reaction products were separated.

The modification of the catalytic systems by ethriolphosphite (Table 3) sharply increases the reaction rate at a high level of selectivity with respect to the target product, and increased selectivity persists after the recycle only for polyethyleneimine.

The earlier<sup>8</sup> study of the influence of P/Rh on the catalytic properties of the  $\text{RhCl}_3$ –polyethyleneimine system in the hydroformylation of but-2-ene showed that a maximum selectivity to 2-methylbutanal is observed already at the ratio P/Rh = 2 and remains unchanged with the further increase in this ratio. The catalytic system retains its properties after the reaction products were separated (see Table 3). When the reaction is completed, ethriolphosphite remains in a complex, and no replenishment of an aqueous layer with a ligand is required in the case of continuous hydroformylation of but-2-enes.

In the case of homogeneous catalysis, deactivation is often ascribed to the ability of mononuclear centers to associate forming clusters inactive in hydroformylation,<sup>9</sup> whereas under the conditions of phase transfer catalysis this can be related to transfer of the catalyst between phases controlled by the hydrophilic-hydrophobic balance of the system. Polycations, being potential macroligands of rhodiumcarbonyl complexes, are of interest,

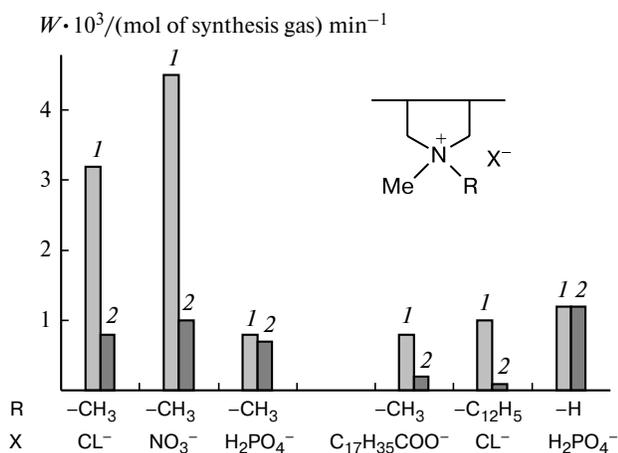
**Table 3.** Hydroformylation of olefins in the presence of catalytic systems Rh—macroligand modified by ethriolphosphite\*

Olefin	Macroligand L	Catalytic properties of Rh—L modified by ethriolphosphite (P/Rh = 9)					
		Cycle I			Cycle II		
		$\tau$ /h	$W \cdot 10^3$ /mol min <sup>-1</sup>	<i>S</i> (%)	$\tau$ /h	$W \cdot 10^3$ /mol min <sup>-1</sup>	<i>S</i> (%)
But-2-ene	PEI	0	0.2	99*	0	0.2	99*
	WPC	1	0.6	98*	7.0	1.0	77*
	PHP	1	1.4	98*	0.5	0.9	78*
Hex-1-ene	PEI	0	0.1	66**	0	0.09	62**
	WPC	0	2.7	69**	0	1.1	43**
	PHP	0	0.9	69**	0	1.1	41**

\* See Note to Table 2.

because their structure contains quaternary ammonium groups. This allows one to control the hydrophilic-hydrophobic balance by introducing different counterions and radicals into the polycation structure and by changing in the pH or introducing additional low-molecular electrolytes.

The study of the influence of the nature of counterions and radicals at the nitrogen atom in the polycation on the rate of hydroformylation of hex-1-ene in the presence of the macrocomplexes (Fig. 1) showed that the chosen systems have a fairly high activity, which for a macroligand with the nitrate counterion approaches that of conventional homogeneous catalysts. However, the activity decreases sharply in some cases of recycling the aqueous catalytic layer. For example, when the stearic acid residue is introduced as a counterion, the activity loss



**Fig. 1.** Influence of the nature of the counterion and hydrocarbon radical in the polycation structure on the activity of the RhCl<sub>3</sub>—polycation catalytic system in hex-1-ene hydroformylation: 1, starting complex; 2, complex after separation of the reaction products. Conditions: *T* = 90 °C, *P* = 6 MPa (CO : H<sub>2</sub> = 1), *p*-xylene—water, [Rh] = 8.7 · 10<sup>-4</sup> mol L<sup>-1</sup>.

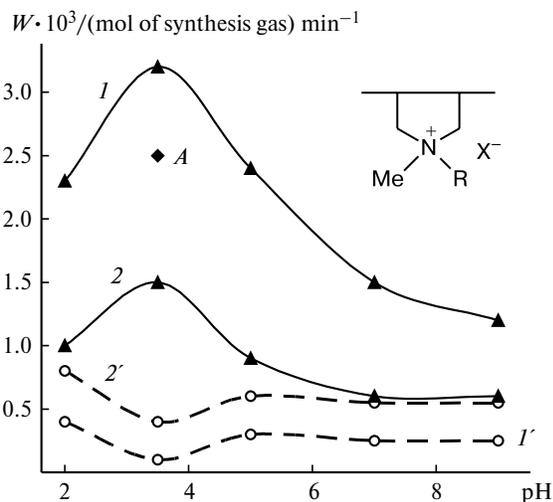
achieves 78%. This occurs due to the redistribution of catalytically active complexes between the organic and aqueous phases.

The replacement of the CH<sub>3</sub> group by a dodecyl radical also results in the activity loss after recycling the aqueous catalytic layer, and only the replacement of the CH<sub>3</sub> group by a hydrogen radical stabilizes the catalytic system. It is known that polycations exist in the dissociated or nondissociated state, depending in the pH, and the introduction of low-molecular electrolytes results in the formation of systems with developed intra- and intermolecular interactions.<sup>10,11</sup>

All catalytic systems under study exhibit an extreme character of the dependence of the hydroformylation rate on the pH with a maximum at pH 3–4 (Fig. 2). In this case, only in the presence of PHP containing a hydrophilic H radical, the catalytic system retains stable operation within an interval pH 6–9, *i.e.*, completely retains its properties in the recycle of the aqueous phase. The activity decreased only in a region of pH 3–4. This is mainly related to the redistribution of the catalytic system between the organic and aqueous phases. The recycle of the organic layer manifests a rather high activity in the hydroformylation of hex-1-ene (see Fig. 2).

In the most cases, the addition of a low-molecular electrolyte as mono-, bi-, and tribasic salt to the system affects the activity of Rh—polycation catalytic systems.<sup>12</sup> The best result was obtained for the Rh—PHP system in the presence of Na<sub>3</sub>PO<sub>4</sub>. The catalytic system retains its properties in a series of successive experiments with intermediate separation of the reaction products from the aqueous catalytic layer.

Thus, the catalytic system based on RhCl<sub>3</sub> and polycations of diallylic structure possesses a high activity in the hydroformylation of hex-1-ene to enantialdehyde in a water—organic solvent system, although its selectivity toward the target product is low (42%).

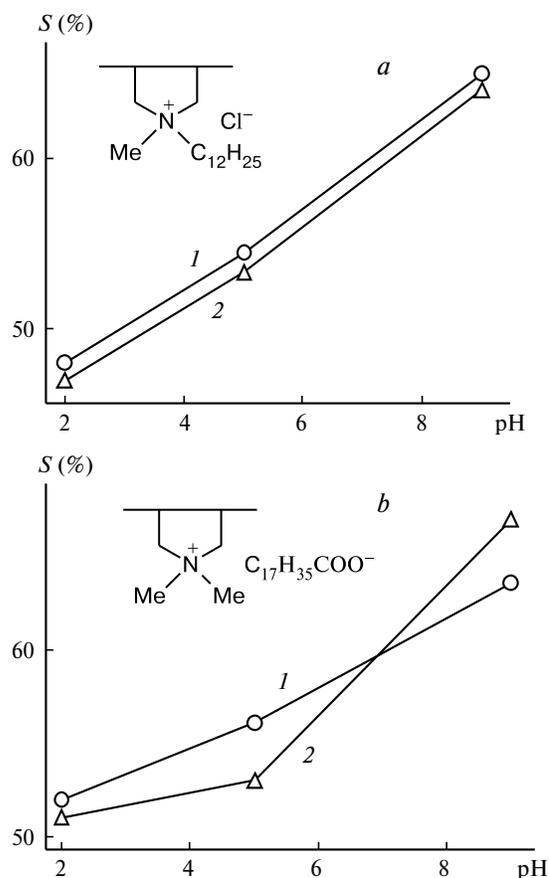


**Fig. 2.** Influence of the pH of the medium on the rate of hex-1-ene hydroformylation in the presence of a  $\text{RhCl}_3$ -based catalytic system and polycations:  $\text{X} = \text{Cl}^-$ ,  $\text{R} = \text{Me}$  (*1*, *1'*),  $\text{X} = \text{H}_2\text{PO}_4^-$ ,  $\text{R} = \text{H}$  (*2*, *2'*); *1*, *2*, starting complex; *1'*, *2'*, complex after separation of the reaction products; *A* is the recycle of the organic layer. Conditions:  $T = 90^\circ\text{C}$ ,  $P = 6\text{ MPa}$  ( $\text{CO} : \text{H}_2 = 1$ ), *p*-xylene–water,  $[\text{Rh}] = 8.7 \cdot 10^{-4}\text{ mol L}^{-1}$ .

A conventional<sup>13</sup> method for suppression of the isomerizing ability of the rhodiumcarbonyl catalysts envisages their modification by organophosphorus ligands. In addition, a nontraditional route<sup>14</sup> of selectivity control is possible for phase transfer catalysis, in particular, introducing into the reaction zone quaternary ammonium salts with long-chain radicals that create steric hindrance at the rhodium atom. This route makes it possible to form a spatial structure of the macrocomplexes preferential for the formation of normal aldehyde. When a stearic acid residue was introduced into the structure of quaternary ammonium groups as a counterion or long-chain hydrocarbon radical ( $\text{R} = \text{C}_{12}\text{H}_{25}$ ), a ~50% selectivity with respect to *n*-aldehyde was achieved at pH 3.4.<sup>15</sup> When the pH increases to 8–9, the selectivity increases to ~65% (Fig. 3). Under these conditions, due to organic solvent affinity, long-chain radicals are arranged perpendicularly to the interface surface to create a "corridor" effect (Scheme 1). The selectivity remains unchanged for the aqueous phase recycle in the whole pH interval.

The obtained results make it possible to develop a new version of the technology for hex-1-ene hydroformylation to enantialdehyde under the phase transfer conditions using a catalytic system based on  $\text{RhCl}_3$  and polycations of diallyl structure.

Natural polymers, such as chitosan and chitin, and synthetic polymers, *viz.*, styrene copolymers containing pyridylmaleimide (STPM) and 4-*N*-pyrrolidinopyridine (STPP) groups in the main chain, are of substantial interest for immobilization of metal complexes. These polymers possess high thermal stability and basicity ( $\text{p}K_{\text{B}} = 9.9$

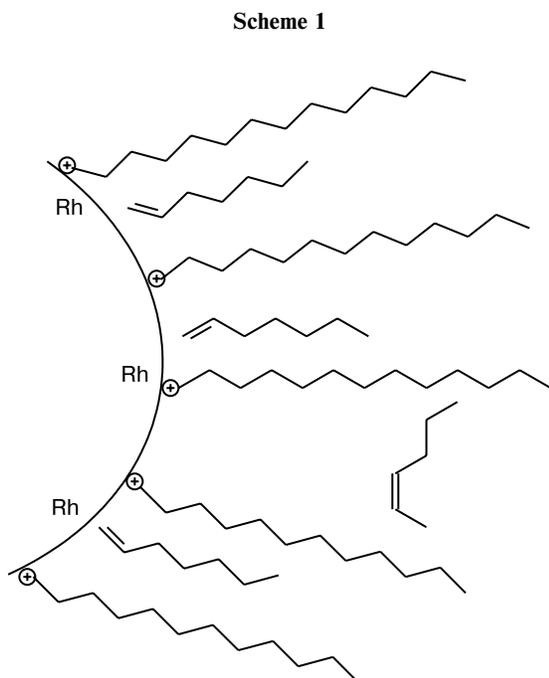


**Fig. 3.** Influence of the pH of the medium on the selectivity of hex-1-ene hydroformylation in the presence of a  $\text{RhCl}_3$ -based system and polycations:  $\text{X} = \text{Cl}^-$ ,  $\text{R} = \text{C}_{12}\text{H}_{25}$  (*a*),  $\text{X} = \text{C}_{17}\text{H}_{35}\text{COO}^-$ ,  $\text{R} = \text{Me}$  (*b*); *1*, starting complex; *2*, complex after separation of the reaction products. Conditions:  $T = 70^\circ\text{C}$ ,  $P = 6\text{ MPa}$  ( $\text{CO} : \text{H}_2 = 1$ ), *p*-xylene–water,  $[\text{Rh}] = 8.7 \cdot 10^{-4}\text{ mol L}^{-1}$ .

at  $20^\circ\text{C}$  for low-molecular pyrrolidinopyridine<sup>16</sup> and  $\text{p}K_{\text{B}} = 9$  for chitosan).

The photoelectron spectra of the synthesized rhodium macrocomplexes exhibit an increase in the bond energy of the  $\text{N}(1s)$  nitrogen atoms of the pyridine rings compared to the energy of these atoms in the initial polymers. The bond energy of the aliphatic  $\text{N}(1s)$  nitrogen atoms remains unchanged upon complex formation. This type of behavior of bond energy indicates that the complexation of rhodium to polymeric ligands proceeds at the nitrogen atoms of the pyridine rings. This is confirmed by an increase in frequencies of stretching vibrations of the carbon–nitrogen bond of the pyridine ring in the FTIR spectra of the macrocomplexes due to a decrease in the conjugation in the ring.<sup>17</sup>

It was found that different amounts of rhodium are involved in complex formation during the same time interval, depending on the structure of the initial polymer.



Based on the amount of rhodium adsorbed from solution, the polymers can be arranged in the following activity series:

Chitosan = STPP > chitin > STPM.

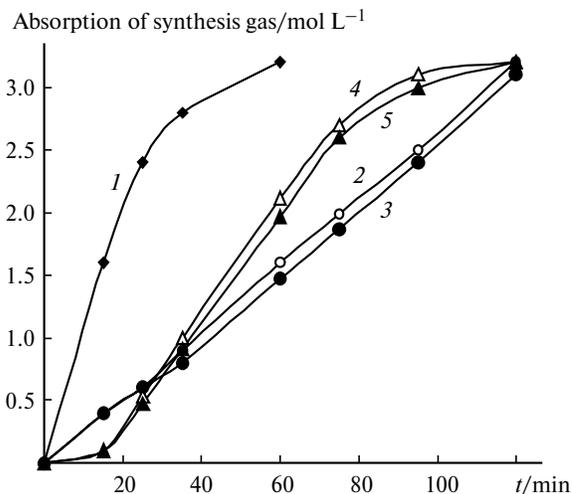
The polymers form the following basicity order:

STPP > chitosan >> chitin > STPM.

Therefore, an increase in the donor properties of the nitrogen atom enhances the activity in complex formation reactions.

The study of the influence of the polymeric ligand structure on the catalytic properties of the rhodium macrocomplex in hex-1-ene hydroformylation showed that all catalytic systems under study are active in this reaction. However, hydroformylation in the presence of the STPP- and chitosan-based catalysts occurs with a higher rate. These catalysts exhibit an induction period, whereas no induction period is observed in the case of STPM and chitin. The presence of an induction period can be explained by different electron states of the nitrogen atom in the polymers. The transition of inactive  $\text{Rh}^{\text{III}}$  in  $[\text{RhCl}_3 \cdot \text{L}]$  to catalytically active mononuclear species of  $\text{Rh}^{\text{I}}$  is facilitated when the coordination sphere of the metal contains ligands with stronger acceptor properties (STPM or chitin), while the presence of strongly donating ligands (STPP or chitosan) impedes this process, resulting in the appearance of an induction period.

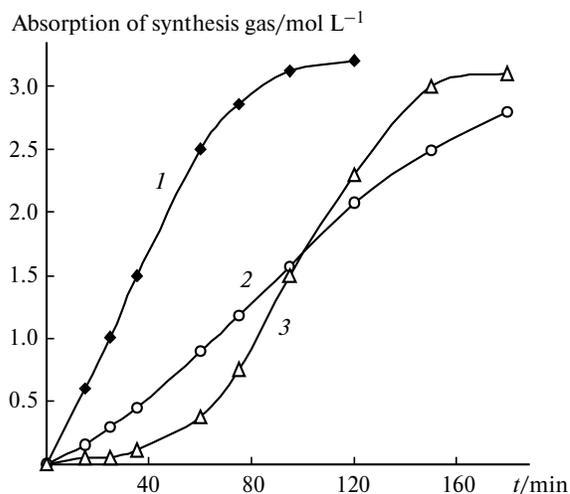
For the hydroformylation of low-reactivity olefins (but-2-enes and isobutene), as for the transformations of hex-1-ene, the reaction rate increases and an induction period appears in the presence of reduced species. The



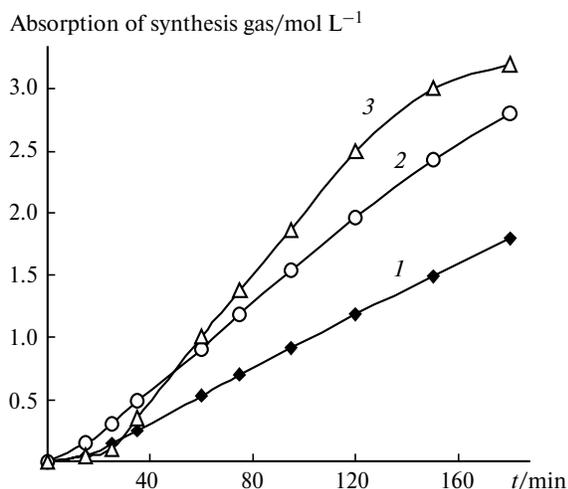
**Fig. 4.** Hydroformylation of hex-1-ene in the presence of catalytic systems: 1,  $\text{acacRh}(\text{CO})_2$ -ethriolphosphite (homogeneous conditions); 2,  $\text{RhCl}_3$ -chitin; 3,  $\text{RhCl}_3$ -STPM; 4,  $\text{RhCl}_3$ -STPP; 5,  $\text{RhCl}_3$ -chitosan. Conditions:  $T = 90^\circ\text{C}$ ,  $P = 6\text{ MPa}$  ( $\text{CO} : \text{H}_2 = 1$ ),  $[\text{Rh}] = 8.7 \cdot 10^{-4}\text{ mol L}^{-1}$ , solvent tridecane.

induction period increases in the series  $\alpha$ -olefins < isoolefins <  $\beta$ -olefins.

Thus, all catalytic systems exhibit high activity in the hydroformylation of medium-molecular olefins. However, the reaction rate for high-reactivity hex-1-ene is lower (Fig. 4) than that for the traditional homogeneous catalytic system ( $\text{Rh}, \text{P}$ ), while the situation changes in the case of low-reactivity olefins. For the hydroformylation of but-2-enes, the heterogenization of the rhodium complexes makes it possible to perform hydroformylation with



**Fig. 5.** Hydroformylation of but-2-enes in the presence of catalytic systems: 1,  $\text{acacRh}(\text{CO})_2$ -ethriol phosphite (homogeneous conditions); 2,  $\text{RhCl}_3$ -STPM; 3,  $\text{RhCl}_3$ -STPP. Conditions:  $T = 90^\circ\text{C}$ ,  $P = 6\text{ MPa}$  ( $\text{CO} : \text{H}_2 = 1$ ),  $[\text{Rh}] = 8.7 \cdot 10^{-4}\text{ mol L}^{-1}$ , solvent *p*-xylene.



**Fig. 6.** Hydroformylation of isobutene in the presence of catalytic systems: 1,  $\text{acacRh}(\text{CO})_2$ –ethriolphosphite (homogeneous conditions); 2,  $\text{RhCl}_3$ –STPM; 3,  $\text{RhCl}_3$ –STPP. Conditions:  $T = 90^\circ\text{C}$ ,  $P = 6\text{ MPa}$  ( $\text{CO} : \text{H}_2 = 1$ ),  $[\text{Rh}] = 8.7 \cdot 10^{-4}\text{ mol L}^{-1}$ , solvent *p*-xylene.

a rate close to that in homogeneous systems (Fig. 5), whereas the hydroformylation of isobutylene in the presence of polymeric catalyst occurs with a rate much higher than that in the case of homogeneous catalysis (Fig. 6).

The results of studying the stability of the catalytic system showed that the rhodium-containing polymeric system retains its properties when stored in the environment of the synthesis gas at  $200^\circ\text{C}$ , which is an advantage of this system over homogeneous rhodium phosphite catalysts retaining their stability at temperatures not higher than  $120$ – $130^\circ\text{C}$ .

Thus, the catalytic system based on  $\text{RhCl}_3$  and styrene copolymer with 4-*N*-pyrrolidinopyridine groups in the main chain is capable of performing isobutene hydroformylation to isovaleraldehyde under the conditions where traditional homogeneous catalysts exhibit low activity. The catalytic system retains its properties in a series of successive cycles with intermediate catalyst separation from the reaction products.

## References

1. P. Pino, F. Piacenti, and M. Bianchi, *Organic Synthesis via Metal Carbonyls*, Eds I. Wender and P. Pino, Wiley, New York, 1977, **2**, 43–197.
2. V. Yu. Gankin and G. S. Gurevich, *Tekhnologiya oksosinteza [Technology of Oxo Synthesis]*, Khimiya, Leningrad, 1981, 272 (in Russian).
3. A. F. Borowski, D. J. Cole-Hamilton, and G. Wilkinson, *Nouv. J. de Chimie*, 1978, **2**, 137.
4. A. D. Pomogailo, *Kataliz immobilizovannymi kompleksami [Catalysis by Immobilized Complexes]*, Nauka, Moscow, 1991 (in Russian).
5. N. V. Kolesnichenko, M. V. Sharikova, N. A. Murzabekova, N. A. Markova, and E. V. Slivinskii, *Neftekhimiya*, 1994, **34**, 226 [*Petroleum Chem.*, 1994, **34** (Engl. Transl.)].
6. G. V. Terekhova, N. V. Kolesnichenko, E. D. Alieva, N. A. Markova, N. I. Trukhmanova, E. V. Slivinskii, and N. A. Plate, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1673 [*Russ. Chem. Bull.*, 1996, **45**, 1583 (Engl. Transl.)].
7. N. A. Markova, Ph. D. (Chem.) Thesis, Moscow, 1989, 142 pp. (in Russian).
8. M. V. Sharikova, N. A. Markova, N. V. Kolesnichenko, A. T. Teleshev, E. V. Slivinskii, and L. A. Vytnova, *Neftekhimiya*, 1996, **36**, 422 [*Petroleum Chem.*, 1996, **36** (Engl. Transl.)].
9. E. V. Slivinskii, R. A. Aronovich, V. I. Kurkin, G. A. Korneeva, A. K. Kobayakov, N. N. Rzhhevskaya, T. B. Ushakova, and S. M. Loktev, *Neftekhimiya*, 1991, **31**, 797 [*Petroleum Chem.*, 1991, **31** (Engl. Transl.)].
10. L. M. Bowman and C. V. Cha, *J. Polym. Sci.*, 1979, **7**, 167.
11. E. Kokufuta, S. Kokubo, and S. Iwai, *Chem. Abstrs*, 1977, 44129D.
12. N. V. Kolesnichenko, M. V. Sharikova, N. A. Murzabekova, N. A. Markova, and E. V. Slivinskii, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1943 [*Russ. Chem. Bull.*, 1995, **44**, 1863 (Engl. Transl.)].
13. N. V. Kolesnichenko, N. A. Markova, E. T. Teleshev, and E. V. Slivinskii, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 702 [*Russ. Chem. Bull.*, 1999, **48**, 698 (Engl. Transl.)].
14. M. J. H. Russell, *Platinum Metal Rev.*, 1988, **32**, 179.
15. N. V. Kolesnichenko, M. V. Sharikova, N. A. Murzabekova, N. A. Markova, and E. V. Slivinskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1968 [*Russ. Chem. Bull.*, 1996, **45**, 1866 (Engl. Transl.)].
16. G. Hoflie, W. Steglich, and H. Forbruggen, *Angew. Chem.*, 1978, **90**, 603.
17. N. V. Kolesnichenko, E. D. Alieva, N. A. Markova, N. I. Trukhmanova, Z. D. Voronina, E. V. Slivinskii, and N. A. Plate, *Neftekhimiya*, 2001, **341**, 354 [*Petroleum Chem.*, 2001, **341** (Engl. Transl.)].

Received July 5, 2004;  
in revised form October 14, 2004