Hydroformylation of olefins in the presence of rhodium carbonyl catalysts immobilized on polymeric pyrrolidinopyridines

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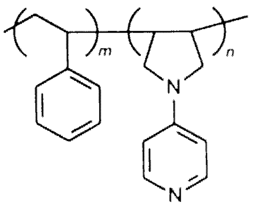
The hydroformylation of olefins in the presence of catalytic systems based on $RhCl_3$ and polymeric pyrrolidinopyridines was studied. It was shown that the catalytic system has high activity in the hydroformylation of isobutylene under conditions when the activity of conventional homogeneous catalysts is low. The polymeric catalysts are also thermostable. The effect of solvents on the catalytic properties of the system was studied.

Key words: hydroformylation, polymers, isobutylene, rhodium, Rh-catalysts.

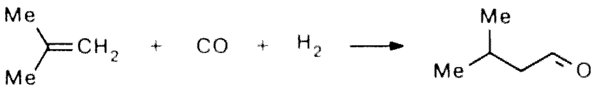
One of the promising ways to increase the stability of rhodium carbonyl catalysts of olefin hydroformylation is to use rhodium complexes immobilized on polymeric carriers. It is of interest to use a copolymer of styrene with 4-*N*-pyrrolidinopyridine units in the main chain as a carrier. Previously,[1] it was shown that it is possible to use such polymers as macromolecular catalysts in the acylation reaction. Since the nitrogen atom in the pyrrolidinopyridine fragment of such a copolymer has a high basicity, one can expect that this matrix not only will firmly hold the rhodium atoms, but it will also affect their catalytic properties.

In the present work we investigated the hydroformylation of isobutylene and hexene-1 in the presence of catalytic systems based on $RhCl_3$ and the copolymer of styrene with 4-*N*-pyrrolidinopyridine (poly-SPP) with molecular mass 70000. The general formula of the polymer is:



n = *m*

Additionally, the effect of solvents on the hydroformylation of isobutylene (IB) to isovaleric aldehyde (IVA) was studied:



The data obtained were compared with the results of the homogeneous hydroformylation of isobutylene in the presence of $Rhacac(CO)_2$, modified by etriol phosphite (ETRO).

Experimental

The experiments were carried out in a glass reactor placed in an autoclave of stainless steel following the procedure described previously.[2] The installation was additionally equipped with a metering device for the introduction of olefin.

Hydroformylation was conducted at 120 °C, 6 MPa, $CO : H_2 = 1 : 1$ (mol.), $[Rh] = 2.3 \cdot 10^{-4}$ mol L^{-1}; *para*-xylene was used as the solvent. A catalyst containing $1.06 \cdot 10^{-2}$ g of Rh per 1 g of polymer was used in all experiments. Calculations were performed per 1 L of the reaction mixture. The reaction was conducted until 95 % conversion of olefin. The reaction rate was monitored by the amount of the consumed synthesis gas, which, in turn, was determined by the pressure drop in the calibrated vessel, from which gas was delivered to the autoclave as was consumed.

The reaction products were analyzed on a Chrom-5 chromatograph (capillary column, 50 m; phase — PEG 20 m, helium as carrier gas, $T = 110$ °C).

$RhCl_3 \cdot 4H_2O$ and $Rhacac(CO)_2$ were used as precursors of the rhodium catalyst of hydroformylation. Rhodium acetylacetonate,[3] etriol phosphite,[4] and the copolymer of styrene with 4-*N*-pyrrolidinopyridine[1] were prepared using known procedures. Carbon oxide was obtained *via* dehydration of formic acid by sulfuric acid. The synthesis gas was prepared by mixing the electrolytic hydrogen and carbon oxide, and was subjected to a two-step purification from oxygen to $[O_2] = 10^{-6}$ % on Cu/SiO_2 and Cr_2O_3/SiO_2 catalysts.

Results and Discussion

As can be seen from Fig. 1 (curves *1* and *2*), the hydroformylation of isobutylene in the presence of

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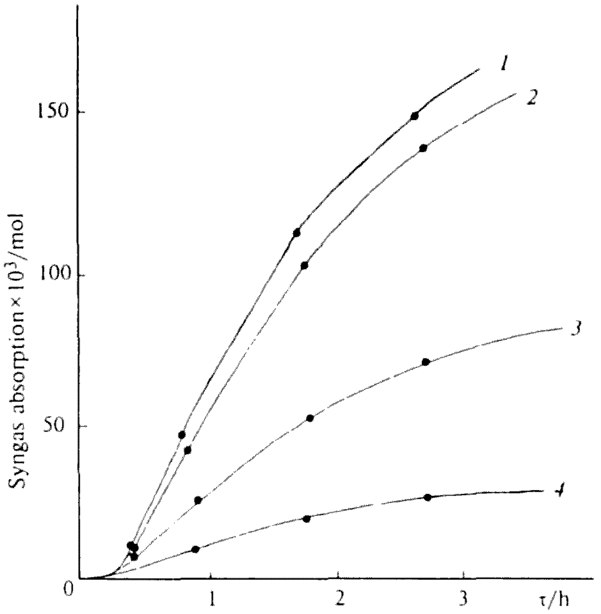

Fig. 1. Hydroformylation of isobutylene in the presence of catalytic systems: *1*, $RhCl_3$—poly-SPP (poly-SP/Rh = 2); *2*, $Rhacac(CO)_2$—poly-SPP; *3*, $RhCl_3$—PP; *4*, $Rhacac(CO)_2$ + ETRO (P/Rh = 9) (T = 120 °C, P = 6 MPa, CO : H_2 = 1 : 1, mol.)

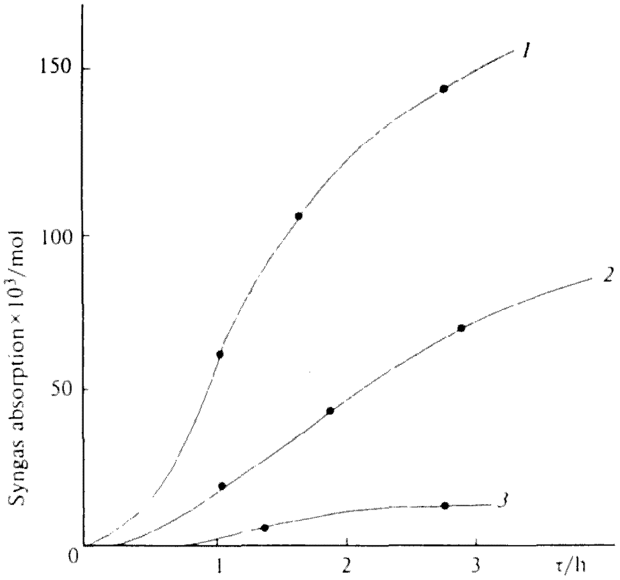

Fig. 2. Hydroformylation of hexene-1 in the presence of catalytic systems: *1*, $Rhacac(CO)_2$ + ETRO (P/Rh = 9); *2*, $RhCl_3$—poly-SPP (poly-SP/Rh = 2); *3*, $RhCl_3$—PP (PP/Rh = 2) (T = 120 °C, P = 6 MPa, CO : H_2 = 1 : 1, mol.)

$RhCl_3$—poly-SPP proceds at a high rate independently of the catalyst precursor. Catalytic systems do not lose their activity after the reaction products are eliminated and recycled. A different picture is observed in homogeneous hydroformylation in the presence of $Rhacac(CO)_2$, modified by ETRO. In this case the hydroformylation of isobutylene proceeds at a low rate (Fig. 1, curve *4*).

The hydroformylation of hexene-1 (Fig. 2, curve *2*) in the presence of $RhCl_3$—poly-SPP has an induction period; in this case the synthesis rate is substantially lower than with the use of $Rhacac(CO)_2$ + ETRO (Fig. 2, curve *1*). The hydroformylation of hexene-1 proceeds at a higher rate (Fig. 2, curve *1*) than the hydroformylation of isobutylene in the presence of conventional Rh-catalysts (Fig. 1, curve *4*). The picture is changed by heterogenization of the Rh-complexes: hydroformylation of hexene-1 in the presence of the $RhCl_3$—poly-SPP system proceeds more slowly than hydroformylation of isobutylene. This inversion occurs for a number of reasons, in particular, because of the different affinity of the polymer for the substrate, the high basicity of nitrogen in the pyrrolidinopyridine fragment,[1] *etc.* In this connection, it was of interest to compare hydroformylation of olefins in the presence of heterogeneous $RhCl_3$—poly-SPP catalysts with hydroformylation in the presence of the rhodium complex of pyrrolidinopyridine (PP), a low-molecular analog of the polymeric catalytic systems under study. The rate of hydroformylation of isobutylene and hexene-1 in the presence of $RhCl_3$—PP (Figs. 1 and 2, curves *3*), all things being equal, was established to be significantly lower than in the presence of $RhCl_3$—poly-SPP. In this case hydroformylation of isobutylene also proceeds at a higher rate than hydroformylation of hexene-1. The result obtained allows one to assume that the high basicity of the nitrogen atom in the pyrrolidinopyridine fragment of the copolymer significantly affects the ratio of the rates of hydroformylation of hexene-1 and isobutylene. The fact that the rates of hydroformylation of olefins in the presence of the $RhCl_3$—PP catalytic system are lower than that with a polymeric catalyst can be associated with the fact that the amount of pyrrolidinopyridine is insufficient to prevent transition of the active rhodium complex into polynuclear complexes.[5]

The development of heterogeneous catalytic systems for hydroformylation makes it possible to use processes with relatively drastic temperature regimes. In this case, the thermal stability of heterogeneous catalysts is one of the decisive factors of their application. In this connection the stability of the $RhCl_3$—poly-SPP catalytic system was studied: the rates of hydroformylation of isobutylene before and after storage of the catalytic system under the synthesis gas at various temperatures were compared. Under these conditions unmodified rhodium carbonyls are known to aggregate[5] into inactive polynuclear complexes.

Our experiments showed (Table 1) that the catalytic system $RhCl_3$—poly-SPP remains stable after storage under the synthesis gas at 200 °C, which is its greatest advantage over homogeneous rhodium-phosphite catalysts stable at temperatures not higher than 120—130 °C.[6]

The effect of solvents on the catalytic properties of $RhCl_3$—poly-SPP was studied. As can be seen from

Table 1. Hydroformylation of isobutylene in the presence of the catalytic system $RhCl_3$—poly-SPP (120 °C, 6 MPa), preliminary kept for 20 h under the synthesis gas in the absence of olefin

T/°C[a]	$r_0 \cdot 10^2$/mol L^{-1} min^{-1} [b]
90	1.3
120	1.3
150	1.2
200[c]	0.9

[a] Storage temperature.
[b] For the starting catalyst $r_0 = 1.3 \cdot 10^{-2}$ mol L^{-1} min^{-1}.
[c] Storage time 3 h.

Table 2. The effect of the solvent on the catalytic properties of $RhCl_3$—poly-SPP in the hydroformylation of isobutylene (90 °C, 6 MPa)

Solvent	Induction period/h	$r_0 \cdot 10^2$ /mol L^{-1} min^{-1}
para-Xylene	0.25	6.4
Pyridine	0.1	20.1
Acetone	0.0	1.5
Octanol	3.5	1.9
Hexane	2.0	1.8

Table 3. The effect of the reaction medium on the hydroformylation of isobutylene in the presence of the system $RhCl_3$—poly-SPP (120 °C, 6 MPa)

Reaction medium		Induction period/h	$r_0 \cdot 10^2$ /mol L^{-1} min^{-1}
Components	Composition (vol. %)		
para-Xylene	100	0.25	6.4
para-Xylene Pyridine	84 16	0.20	7.2
para-Xylene Pyridine Water	68 16 16	2.50	7.8

Table 2, replacing *para*-xylene with pyridine results in a sharp increase in the reaction rate and in a decrease in the induction period. The reaction rate is significantly decreased in the presence of other solvents. The high activity of $RhCl_3$—poly-SPP in the presence of pyridine and *para*-xylene can be explained by the good swelling of the polymer in these solvents, which makes it easier for the substrate access to active centers.

The effect of solvent polarity on the catalytic properties of $RhCl_3$—poly-SPP in the hydroformylation of isobutylene was also studied. The medium polarity was changed by adding water or pyridine to *para*-xylene, in which the polymer readily swells. As can be seen from Table 3, the introduction of pyridine results in a decrease in the induction period and in an insignificant increase in the reaction rate. The use of the *para*-xylene—pyridine—water mixture only increases the induction period. In all cases studied nearly 100 % selectivity of isovaleric aldehyde formation was observed.

Thus, the use of polymeric pyrrolidinopyridines as macromolecular ligands for rhodium complexes not only allows one to increase the efficiency of the hydroformylation process, but also to enhance the number of chemicals obtained by this method.

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