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Selectivity of catalytic systems $RhCl_3$ • polycation in hydroformylation of hex-1-ene under conditions of biphase catalysis

N. V. Kolesnichenko, M. V. Sharikova, T. Kh. Murzabekova, N. A. Markova, and E. V. Slivinskii*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

Approaches to increasing the selectivity of water-soluble catalytic systems based on $RhCl_3$ and polycation in hydroformylation of hex-1-ene were studied. The introduction of a long-chain alkyl radical into the polycation or the use of a higher fatty acid anion results in an increase in the selectivity of the catalytic system at pH > 7 with respect to *n*-aldehyde to 60 %. This effect is presumably associated with the suppression of isomerization processes due to steric hindrances.

Key words: hydroformylation, water-soluble rhodium catalyst, polycations.

Carbonylation reactions are the basis for industrial processes of preparation of aldehydes, alcohols, and acids.[1] Recently, different variants are being developed of a new technology for hydroformylation using catalysts dissolved in an aqueous phase, while a substrate and reaction products are present in an organic phase. This method of hydroformylation under biphase conditions simplifies isolation of reaction products from the catalyst and makes it possible to involve high-molecular olefins in this process.[2]

Based on the commonly accepted mechanism of hydroformylation on Rh-catalysts,[3,4] the distribution of aldehydes over isomers can be "formed" at the reversible stage of the transition of the π-complex of metal hydrocarbonyl with olefin to the σ-complex, at the stage of isomerization of alkyl and acyl complexes, and at the stage of isomerization of olefin. It is accepted[3,4] that the steric factor is determining in all cases.

Rhodium complexes modified by organophosphorus ligands are usually used for suppression of isomerization.[3] When catalysis is performed in a biphase system, a nontraditional way of controlling the selectivity is possible, in particular, the introduction of quaternary ammonium salts (QAS) with long-chain radicals, which create steric hindrances for the rhodium atom, into the reaction zone.[2]

It has been previously shown[5] that catalytic systems based on $RhCl_3$ and modified by polycations containing quaternary ammonium groups are highly efficient catalysts of hydroformylation of hex-1-ene. However, their selectivity is insufficiently high.

This work studies the possibility of enhancing the selectivity of the $RhCl_3$ · polycation catalytic system in hydroformylation of hex-1-ene under biphase conditions.

Experimental

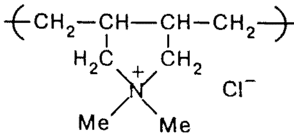
Hydroformylation of hex-1-ene was carried out in an autoclave of stainless steel in the periodic regime with vigorous stirring according to the procedure described previously.[5]

Reaction products were analyzed on a Chrom-5 chromatograph (capillary column, l = 25 m, PEG-20M as phase, helium as carrier gas, T = 120 °C). The content of hydrocarbons in a sample was determined by GLC on a Tsvet chromatograph with a detector of heat conductivity on a column filled with 10 % triethylene glycol butyrate on diatomite, at 50 °C.

Carbon oxide was synthesized by the known method.[5] Synthesis gas was obtained by mixing electrolytic hydrogen and carbon oxide followed by the two-stage purification of the mixture on the Cu/SiO_2 catalyst and Cr_2O_3/SiO_2 sorbent to the residual content of oxygen of 10^{-6} %.

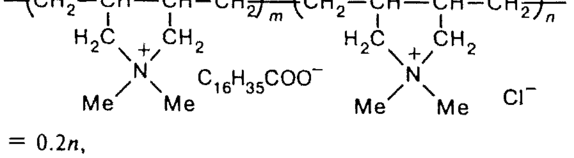
$RhCl_3 \cdot 4H_2O$ ([Rh] = $8.7 \cdot 10^{-4}$ g-at. L^{-1}) and polycations ($2.2 \cdot 10^{-4}$ mol L^{-1}) of the following structure were used as components of the catalytic system:

poly-*N,N*-diallyl-*N,N*-dimethylammonium chloride with molecular weight 30000 is an industrial sample with TU-6-05-2009-86 (**1**):



1 ,

polycation (**2**) obtained in the exchange reaction of **1** with stearic acid:



2 ,

$m = 0.2n$,

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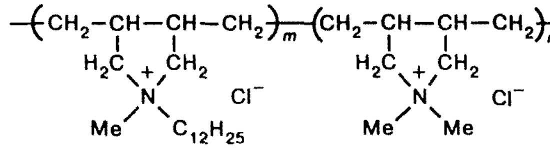
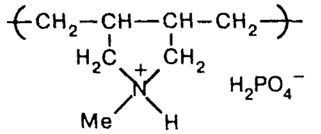
polycation (**3**) synthesized by realkylation of **1** by dodecyl chloride:



3

$m = 0.05 - 0.1n$,

poly-*N*,*N*-diallyl-*N*-methyl aminodihydrophosphate (**4**) obtained by radical photopolymerization of methyldiallylamine in concentrated orthophosphoric acid (molecular weight 50000):



4.

Results and Discussion

Hydroformylation of hex-1-ene results in the formation of a mixture of heptanal (H), 2-methylheptanal (2-MH), and 2-ethylpentanal (2-EP) due to the transformation of both the initial olefin and the product of its isomerization (hex-2-ene).[6]

It is evident that 2-MH can be formed from both hex-1-ene and the isomerized substrate, while 2-EP is the product of hydroformylation of hex-2-ene alone. According to the known mechanism of hydroformylation,[3] 2-EP can be formed at the stage of isomerization of the alkyl complex without elimination of hex-2-ene.

When hex-1-ene is hydroformylated in the presence of the $RhCl_3 \cdot \mathbf{1}$ catalyst in the biphase system, the reaction products at the complete conversion of olefin contain a noticeable amount of 2-EP, which is evidence for the occurrence of the isomerization reaction.

The time dependence of the composition of reaction products of hydroformylation of hex-1-ene is presented in Fig. 1. It can be seen that the selectivity of the catalyst with respect of the formation of *n*-aldehyde remains almost unchanged before hex-2-ene begins to be involved in the hydroformylation. From this time, the selectivity decreases sharply, and its value approaches that for the complete conversion of olefin (43 to 45 %). By conversion we mean the regioselectivity with respect to *n*-heptanal (target product). It was calculated by the formula:

$$S = G/\Sigma \text{ (aldehydes)},$$

where G is the amount of the resulting *n*-heptanal.

Polymeric QAS can be modified by the addition of a long-chain radical into the polymer by realkylation (substitution of the Me group at the nitrogen atom) or by substitution of chlorine for an anion of a higher carboxylic acid. This modification of the polymer structure can result in the appearance of steric hindrances at the rhodium atom upon complex formation.

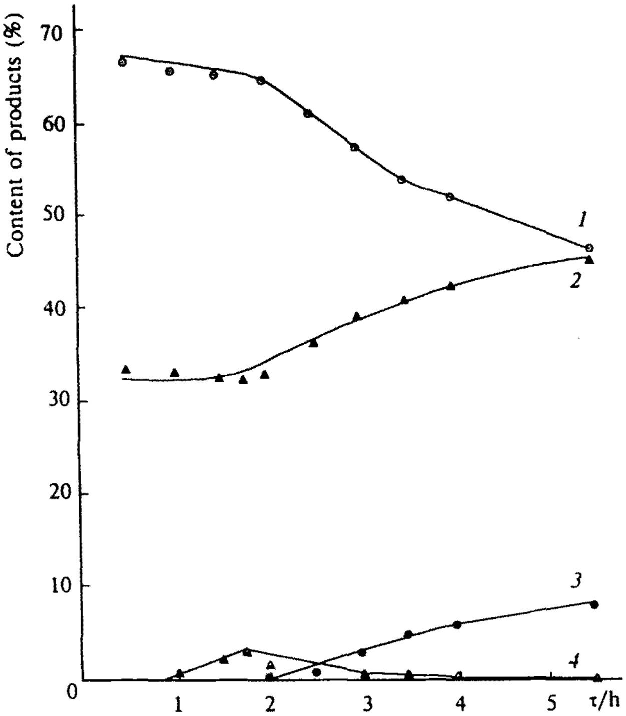


Fig. 1. Time dependences of content of reaction products of hydroformylation of hex-1-ene in the presence of catalyst $RhCl_3 \cdot \mathbf{1}$ (T = 70 °C, p_{CO+H_2} = 6.0 MPa): *n*-heptanal (*1*), 2-methylhexanal (*2*), 2-ethylpentanal (*3*), and hex-2-ene (*4*).

To study the effect of the length of the hydrocarbon radical in QAS on the selectivity of the catalytic system, two samples of a polycation were synthesized: in the first of them, 20 % of Cl^- anions were substituted for anions of stearic acid (polymer **2**), and in the second sample, some Me groups at the nitrogen atoms were substituted for dodecyl groups (polymer **3**). The possibility of substitution *in situ* of chloride anions for anions of carboxylic acids was also studied. Due to the low solubility of organic acids in water, a tenfold excess of them was taken relative to the amount necessary for the complete quaternization of all nitrogen atoms in the polymer. The results are presented in Table 1.

Under the conditions studied, both **2** and **3** exhibit a considerably higher selectivity, which does not substantially change with repeated testing of the aqueous layer after its separation from the reaction products. However, the reaction rate decreases strongly in the presence of recycling because of the partial transition of the catalytic system to the organic phase due to the high affinity of the polymer toward the organic solvent.[5]

Addition *in situ* of organic acids also results in a considerable increase in selectivity with respect to *n*-aldehyde.

It is noteworthy that small amounts of 2-EP (3 to 4 %) were observed in the reaction products un-

Table 1. Hydroformylation of hex-1-ene in the presence of $RhCl_3$ and polycations (T = 70 °C, p_{CO+H_2} 6.0 MPa, pH in aqueous phase 3—4)

Polycation	Degree of substitution (%)	Carboxylic acid added *in situ*	Catalytic properties of initial catalyst: r_0* · 10^3 /mol min^{-1}	Catalytic properties of initial catalyst: S (%)	Catalytic properties with recycling of aqueous layer: r_0* · 10^3 /mol min^{-1}	Catalytic properties with recycling of aqueous layer: S (%)
1	—	—	3.2	41	0.9	41
4	—	—	1.5	43	0.4	42
3	5	—	1.8	51	0.4	48
3	10	—	1.0	55	0.3	56
2	20	—	1.1	54	0.2	55
1	—	Stearic	1.3	53	0.3	58
4	—	Stearic	0.4	58	0.3	56
4	—	Undecanoic	0.4	67	0.1	59

* r_0 is the initial rate of hydroformylation.

der any method of introduction of long-chain radicals into the polycation.

It has been previously established that pH in the aqueous phase exerts a great effect on the catalytic properties of the $RhCl_3$ · **1** systems.[7] In this work, the effect of this indicator on the catalytic properties of the catalysts containing polycations **2** and **3** is studied. The results are presented in Figs. 2—4.

The character of the change in the rate of hydroformylation on pH (see Fig. 2) is analogous for both samples and is usual for such systems.[7] In addition, there is some stabilization of the work of the catalytic systems as pH increases: in the acidic medium, the reaction rate in the presence of recycling of the aqueous phase decreases by 80 %, while at pH = 9 it decreases by 50 %.

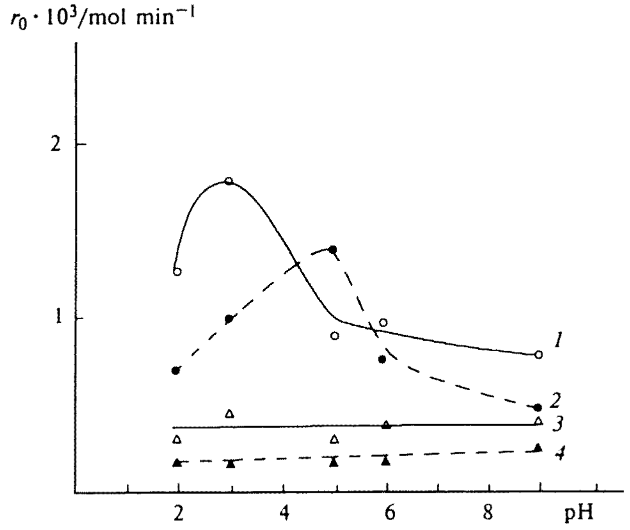


Fig. 2. Effects of pH in aqueous layer on the rate of hydroformylation of hex-1-ene (r_0) in the presence of $RhCl_3$ · **3** (*1, 3*), and $RhCl_3$ · **2** (*2, 4*) for initial catalyst (*1, 2*) and aqueous layer after separation of products (*3, 4*).

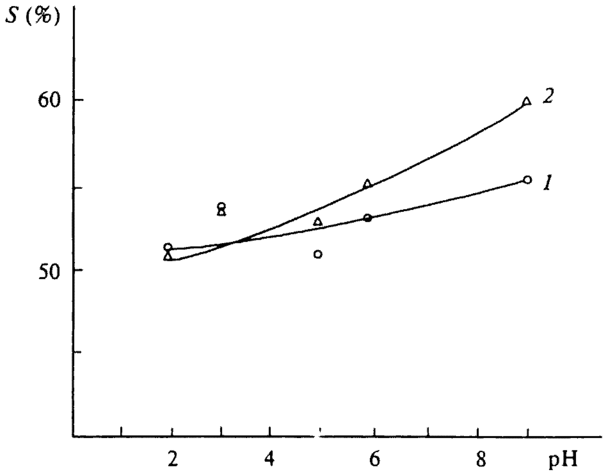


Fig. 3. Effects of pH in aqueous layer on selectivity of catalyst $RhCl_3$ · **2** with respect to formation of *n*-heptanal: *1*, initial sample; *2*, aqueous layer after separation of reaction products.

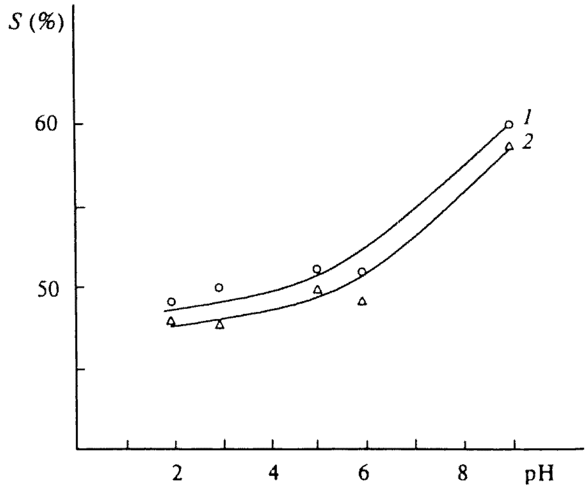


Fig. 4. Effect of pH in aqueous layer on selectivity of catalyst $RhCl_3$ · **3** in hydroformylation of hex-1-ene: *1*, initial sample; *2*, aqueous layer after separation of reaction products.

The selectivity of the catalyst with respect to the formation of *n*-heptanal also increases as pH increases (see Figs. 3 and 4). It reaches 60 % in the pH range from 8 to 9, and no 2-ethylpenatanal is observed in the reaction products. Thus, the selectivities of the $RhCl_3 \cdot \mathbf{2}$ and $RhCl_3 \cdot \mathbf{3}$ catalytic systems are close to that of the $RhCl_3 \cdot \mathbf{1}$ catalyst at the partial conversion of hex-1-ene observed 0.5 h after the beginning of the reaction (see Fig. 1), *i.e.*, at the moment when the distribution of aldehydes over isomeric composition is virtually not complicated by isomerization.

It can be imagined that in the pH range from 8 to 9 a situation is realized in which long-chain radicals, due to their affinity toward an organic solvent, are arranged perpendicularly to the interface in polymers **2** and **3** to create a "corridor effect." Due to this, steric hindrances appear for isomerization of a substrate as well as alkyl and acyl rhodium complexes.

Thus, when ~10 % of long-chain radicals or ~20 % of anions of stearic acid are introduced into the polycation at pH > 7, the selectivity of the catalytic system with respect to the formation of *n*-heptanal increases to 60 % (under similar conditions, the selectivity of the $RhCl_3 \cdot \mathbf{1}$ catalyst is 42 %).

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