

Effect of composition of the aqueous phase on catalytic properties of RhCl_3 modified with a polycation in hydroformylation of 1-hexene

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

Water-soluble catalytic systems based on RhCl_3 and the salts of polycations (poly-*N,N*-diallyl-*N,N*-dimethylammonium chloride and poly-*N,N*-diallyl-*N*-methylaminodihydrophosphate) have been studied. It has been established that the rate of hydroformylation of 1-hexene increases with increasing pH of the aqueous phase. The replacement of the alkyl group at the nitrogen atom with the hydrogen atom in a polycation makes it possible to form a stable catalytic system at $\text{pH} \geq 5$. The addition of low molecular electrolytes (NaCl , Na_2SO_4 , and NaPO_4) also affects the catalytic properties of the studied catalytic systems. Stability of a catalytic system is enhanced with increasing charge of an anion of a low molecular electrolyte, which is, apparently, due to formation of intra- and intermolecular bonds in polyelectrolytes.

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

Hydroformylation of olefins in the presence of water-soluble rhodium catalysts in a two-phase water—organic solvent system makes it possible to perform synthesis of oxygen-containing compounds, from which a catalyst is difficult or impossible to separate under conditions of homogeneous catalysis.¹ In a two-phase system, stability of a rhodium catalyst is determined primarily by its distribution between phases.

The use of water-soluble polymers that contain quaternary ammonium groups (polycations) as components of a catalytic system makes it possible to regulate catalytic properties of the system not only through the replacement of a radical and a counterion at the nitrogen atom² but through change in the composition of the reaction medium as well.

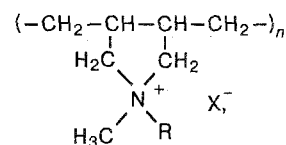
In this work, the effects of pH of an aqueous layer and the nature of the added low-molecular electrolytes such as NaCl , Na_2SO_4 , and Na_3PO_4 on stability of RhCl_3 —polycation systems have been studied.

Experimental

Hydroformylation of 1-hexene was carried out in a stainless steel autoclave in the periodic mode at 70 °C with active stirring. The procedures of the performance of the reaction, analysis, and preparation of synthesis gas were reported previously.²

The pH of the initial solution of the catalyst (an aqueous phase) was 3–4. This value was changed by adding acid or alkali.

$\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ and salts of polycations of the following general formula were used as components of a catalytic system:



where (a) $\text{R} = \text{Me}$, $\text{X} = \text{Cl}$: poly-*N,N*-diallyl-*N,N*-dimethylammonium chloride (PDDAC) with molecular weight of 30000, a commercial sample; (b) $\text{R} = \text{H}$, $\text{X} = \text{H}_2\text{PO}_4$: poly-*N,N*-diallyl-*N*-methylaminodihydrophosphate (PDMAAP) with molecular weight of 50000, which was obtained by a known procedure.²

The hydroformylation rate, which was determined as the number of moles of converted synthesis gas in a unit time, was taken to be a measure of activity of a catalyst.

Stability was estimated from the reaction rate in the repetitive test of an aqueous catalytic layer after separation of the reaction products.

The reduction in stability, the relative decrease in the reaction rate upon recycling a catalyst, was calculated by the following formula:

$$\alpha = \frac{r_{01} - r_{02}}{r_{01}} \cdot 100 \%,$$

where r_{01} and r_{02} are the reaction rates in the presence of the initial catalytic system and after the recycling of the system, respectively.

By storing is meant the stay of rhodium catalyst under conditions of hydroformylation in the absence of olefin for 18 h.

Results and Discussion

We have established that the pH of an aqueous phase has a pronounced effect on the catalytic properties of RhCl_3 modified with PDDAC and PDMAP ($\text{RhCl}_3 \cdot \text{PDDAC}$ and $\text{RhCl}_3 \cdot \text{PDMAP}$, respectively) (Fig. 1). The pH dependence of the reaction rate has an extreme character with a maximum at 3–4. Note that the catalytic system based on PDDAC is unstable throughout the pH range: a decrease in the reaction rate was observed when an aqueous layer was reused after its separation from the reaction products. In the case of PDMAP, stability decreases only in the pH range 3–4, while in the pH range 6–9, the system completely retains its properties when the aqueous layer is reused.

A decrease in stability may be caused by redistribution of the catalytic system between organic and aqueous phases. Actually, as is evident from Fig. 1, when the organic layer was used as the catalyst, hydroformylation proceeds at a rather high rate. Rhodium may pass into an organic layer in the form of unmodified carbonyls or in the form of a complex with the polycation.

In this connection, the organic layer was subjected to storing under reaction conditions in the absence of olefin. Unmodified rhodium carbonyls aggregate to form polynuclear complexes, which are inactive in hydroformylation.³ Storing of the organic layer did not cause the loss in catalytic activity. When the organic layer was used as the catalyst, the rate of hydroformylation of 1-hexene ($T = 70^\circ\text{C}$, $p = 6.0\text{ MPa}$, $\text{CO}/\text{H}_2 = 1$) before and after storing remained unchanged and was $2.3 \cdot 10^{-3}\text{ mol min}^{-1}$. This storing under homogeneous conditions in the presence of unmodified $\text{Rh}_4(\text{CO})_{12}$ caused virtually complete deactivation of the catalyst. In the presence of the initial complex, the rate of hydroformylation of 1-hexene was $6 \cdot 10^{-3}\text{ mol min}^{-1}$; after storing, the rate decreased to $0.4 \cdot 10^{-3}\text{ mol min}^{-1}$.

Therefore, the data obtained provide evidence that, when hydroformylation is performed in a two-phase system, redistribution of the catalyst among phases occurs predominantly in the form of the rhodium complex with the polycation. This process can occur only when the catalytic system partially loses its hydrophilicity, *i.e.*, when its affinity to an organic medium is enhanced.

Apparently, this is determined by the conformational state of the macromolecule because it is known that in an aqueous solution, the polycation dissociates into ions, and the degree of dissociation depends on pH (see Ref. 4). Dissociation is suppressed both in acidic and alkaline media, which leads to twisting of the macromolecule.

It is known^{4,5} that the conformational state of polycations changes not only with pH but also with the presence of low-molecular electrolytes in the system.

In this connection, the effects of the nature and the concentration of the added low-molecular electrolytes on catalytic properties of the $\text{RhCl}_3 \cdot \text{PDDAC}$ and $\text{RhCl}_3 \cdot \text{PDMAP}$ systems in hydroformylation of

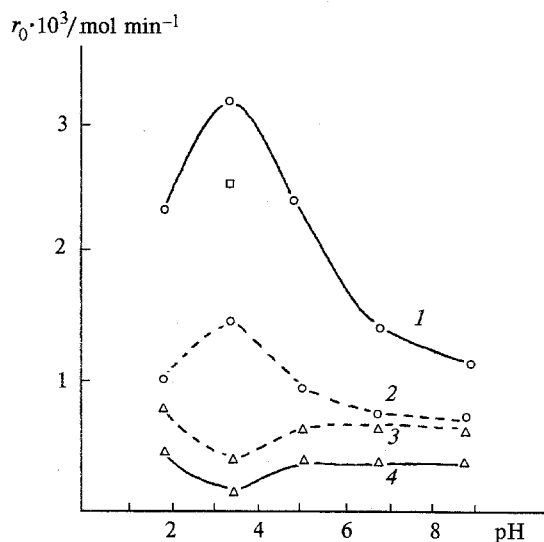


Fig. 1. Effect of pH on the rate of hydroformylation of 1-hexene in the presence of $\text{RhCl}_3 \cdot \text{PDDAC}$ (1, 4) and $\text{RhCl}_3 \cdot \text{PDMAP}$ (2, 3) in the presence of the initial catalyst (1, 2) and an aqueous layer after separation of the products (3, 4). The \square point corresponds to the reaction rate in the presence of a separated organic layer.

1-hexene were studied. For this purpose, the following organic salts were used: NaCl , Na_2SO_4 , and Na_3PO_4 .

Addition of NaCl causes a decrease in activity and a slight increase in stability of the catalytic system (Table 1). The use of Na_2SO_4 has little effect both on activity and stability of the $\text{RhCl}_3 \cdot \text{PDDAC}$ catalytic system. After the experimental run, a black precipitate was formed at the interface.

In the case of Na_3PO_4 , the $\text{RhCl}_3 \cdot \text{PDDAC}$ catalytic system becomes more stable; however, the α value decreases as the concentration increases on reuse of catalyst.

For the $\text{RhCl}_3 \cdot \text{PDMAP}$ system, an addition of Na_3PO_4 also leads to a substantial increase in stability; at pH 5, the catalytic system retains its properties in the set of successive experimental runs with separation of the reaction products from the catalytic aqueous layer after each run.

Different effects of low-molecular electrolytes on the catalytic properties of the $\text{RhCl}_3 \cdot \text{polycation}$ system can be associated with the ability of the anions of electrolytes to exchange ions with a polycation as well as to form intra- and intermolecular bonds in the polycation.⁵ Thus, an addition of NaCl only suppresses dissociation of a polycation, which leads to twisting of the macromolecule. An increase in the reaction rate due to hindered access of reagents to the active center is attributable to this fact. When polyvalent anions are used, inter- and intramolecular salt bridges are formed, which enhance the stability of a catalytic system. This is observed in the case of Na_3PO_4 . However, when Na_2SO_4 is added, no increase in stability is observed, which is, apparently,

Table 1. Effect of the nature of a low-molecular electrolyte and its concentration on catalytic properties of the $\text{RhCl}_3 \cdot \text{PDDAC}$ and $\text{RhCl}_3 \cdot \text{PDMAP}$ systems in hydroformylation of 1-hexene

Poly-electrolyte	Low-molecular electrolyte (A)	Concentration of A, N	pH of initial solution	Reaction rate $\times 10^3/\text{mol min}^{-1}$			$\alpha(\%)$
				Initial complex	Aqueous layer after separation of reaction products		
					Cycle I	Cycle II	
PDDAC	—	—	3.4	3.2	0.2	—	94
«	—	—	5.0	2.4	0.5	—	79
«	NaCl	0.3	3.4	1.1	0.4	—	64
«	«	1.0	«	1.0	0.2	—	80
«	Na ₂ SO ₄	0.1	«	2.4	0.2	—	92
«	«	«	5.0	3.0	0.2	—	93
«	«	0.3	«	1.4	0.2	—	86
«	Na ₃ PO ₄	0.2	3.4	0.5	0.1	—	80
«	«	0.05	5.0	0.8	0.2	—	75
«	«	0.1	«	0.7	0.3	—	57
«	«	0.2	«	0.3	0.2	—	33
PDMAP	—	—	3.4	1.4	0.4	—	71
«	—	—	5.0	0.8	0.6	—	25
«	Na ₃ PO ₄	0.05	3.4	0.4	0.2	—	50
«	«	0.1	«	0.3	0.2	0.15	33
«	«	«	5.0	0.1	0.1	0.1	0

Note. Conditions of hydroformylation: $T = 70^\circ\text{C}$; $p = 6.0\text{ MPa}$; $\text{CO}/\text{H}_2 = 1$.

determined by deactivation of the rhodium catalyst in the presence of sulfate ions.⁶

References

1. M. J. H. Russel, *Platinum Metals Rev.*, 1988, **32**, No. 4.
2. N. V. Kolesnichenko, T. Kh. Murzabekova, N. A. Markova, M. V. Sharikova, E. I. Demina, E. V. Slivinskii, E. A. Vasil'eva, and D. A. Topchiev, *Neftekhimiya* [*Petrochemistry*], 1994, **34**, 226 (in Russian).
3. Yu. B. Kagan, E. V. Slivinskii, V. I. Kurkin, G. A. Korneeva, R. A. Aronovich, I. G. Fal'kov, N. N. Rzhetskaya, and S. M. Loktev, *Neftekhimiya* [*Petrochemistry*], 1985, **25**, 791 (in Russian).
4. L. M. Bowman and C. Y. Cha, *J. Pol. Sci., Pol. Let. Ed.*, 1979, **17**, 167.
5. W. P. Shyluk, *J. Appl. Polym. Sci.*, 1964, **8**, 1663.
6. A. F. Borowsri, D. J. Cole-Hamilton, and G. Wilkinson, *Nouv. J. Chim.*, 1978, **2**, 137.

Received October 20, 1994