Isobutene hydroformylation in catalytic systems based on rhodium compounds and polyelectrolytes

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The catalytic properties of water-soluble systems based on rhodium complexes and polyelectrolytes in isobutene hydroformylation were studied. All of the catalytic systems exhibited an unexpectedly high activity under the conditions where homogeneous hydroformylation virtually did not occur in the presence of conventional rhodium catalysts. A stable catalytic system based on acacRh(CO)₂-PEG complex was proposed, allowing isobutene hydroformylation to be performed with a high activity under mild conditions.

Key words: hydroformylation, water-soluble rhodium-containing catalysts, polyelectrolytes.

A tendency to widen the scope of the products of olefin hydroformylation is presently observed, for example, the hydroformylation of isobutene to isovaleraldehyde, an intermediate product of the synthesis of ethyl α -bromoisovalerate, which is a major component for medical treatment of cardio vascular diseases. However, the hydroformylation of low-activity isobutene using conventional catalytic systems based on Rh complexes and organophosphorus ligands occurs under drastic conditions.¹ In addition, the reaction product can be contaminated by phosphorus compounds. The most active unmodified rhodium carbonyl catalysts, as is known,² undergo deactivation to form polynuclear clusters. This problem can be solved by the development of new technological approaches, for example, performing hydroformylation under biphase conditions (organic solvent-water).3

In this work, we studied the catalytic properties of water-soluble systems based on Rh compounds and polyelectrolytes (PE) in isobutene hydroformylation.

Experimental

Hydroformylation of isobutene was carried out in an autoclave of stainless steel in a periodic regime with vigorous stirring at T = 90 °C and a pressure of 6 MPa. The products of isobutene hydroformylation and preparation of the synthesisgas have previously been described.⁴ The reaction was performed to ~100% conversion of olefin.

The reaction products were analyzed on a Chrom-5 chromatograph (a capillary column with 150 m, PEG 20M as the phase, helium as the carrier gas, 110 °C). Isovaleraldehyde was the only product of the reaction.

 $RhCl_3 \cdot 4H_2O$, acac $Rh(CO)_2$, and the following polyelectrolytes were used as the components of the catalytic system. 1. Water-soluble polycation (WPC) poly-N,N-diallyl-N,Ndimethylammonium chloride



with a molecular weight of 30 000, commercial sample (TU-6-05-2009-86).

2. Poly-*N*, *N*-diallyl-*N*-methylaminodihydrophosphate (PHP)



with a molecular weight of 50 000 obtained by the known procedure.⁴

3. Branched polyethyleneimine (PEI) with a molecular weight of 10 000.

4. Polyethyleneglycol (PEG) with a molecular weight of $20\ 000$.

The concentration of Rh in all experiments was $8.9 \cdot 10^{-4}$ g-at. L⁻¹ (H₂O).

The reaction was studied in the kinetic region. The rates of hydroformylation were the measure of the catalyst activity, being determined as the number of moles of the synthesis-gas transformed over unit time. The stability was estimated from the reaction rates during repeated testing of the aqueous catalytic layer after separation of reaction products.

"Exposure" implies the existence of the Rh catalyst under hydroformylation conditions without olefin for 10 h.

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Results and Discussion

The catalytic properties of the water-soluble Rh complexes based on N- and O-containing PE in isobutene hydroformylation were studied. As can be seen in Fig. 1, all catalytic systems studied exhibit an unexpectedly high activity under conditions where the homogeneous hydroformylation of isobutene in the presence of conventional Rh catalysts virtually does not occur. The RhCl₃-WPC-based catalytic system is most active. However, it is unstable because more than 50%



Fig. 1. Comparative diagram of the rates of isobutene hydroformylation with the catalytic systems $RhCl_3$ -WPC (a), $RhCl_3$ -PHP (b), $RhCl_3$ -PEI (c), $acaCRh(CO)_2$ -PEG (d), and $acaCRh(CO)_2$ -PEG in situ (e) in the presence of the starting catalytic system (1) and during recycling of the aqueous phase (2) (T = 90 °C, p = 6.0 MPa, $[Rh] = 8.9 \cdot 10^{-4}$ g-at. L^{-1} (H₂O), pH₀ 4).



Fig. 2. Effect of the pH of the aqueous layer on the catalytic properties of the Rh-PE-based systems during isobutene hydroformylation: $RhCl_3$ -WPC (1), $RhCl_3$ -PHP (2), $acacRh(CO)_2$ -PEG (3), and $RhCl_3$ -PEI (4).

of its activity is lost during the recycling of the aqueous phase.

The use of the PHP polycation as a macroligand leads to a decrease in the activity of the system, but its stability increases by several times (see Fig. 1). Hydroformylation of isobutene occurs with sufficiently high rates when the $RhCl_3$ -PEI catalytic system is used; however, this system is also insufficiently stable.

The $acacRh(CO)_2$ -PEG catalytic system is most stable at a sufficiently high activity (see Fig. 1). An interesting fact is observed: this system obtained *in situ* (*i.e.*, during the formation of the complex in the reaction zone from separately added PEG and $acacRh(CO)_2$) is almost twofold more active than the complex prepared preliminarily (Table 1). However, its stability is somewhat lower, and a large induction period of the reaction is observed in the presence of this system.

We have previously shown^{4,5} that not only the nature of the polyelectrolyte but also the composition of the aqueous phase strongly affect the properties of the polyelectrolyte-based catalytic Rh systems (Rh—PE) in the hydroformylation of 1-hexene. In this connection, we studied the influence of pH of the aqueous phase on the catalytic properties of the Rh—PE system during the hydroformylation of isobutene. The results obtained are presented in Fig. 2.

As pH increases, the hydroformylation rates decrease with all of the catalysts studied (see Fig. 2). The WPCbased system is most sensitive to a change in pH. The effect of a change in the basicity of the aqueous phase is the lowest in the case of the acacRh(CO)₂—PEG catalyst. Unlike other catalysts, this system is stable within the whole pH range studied.

Thermal stability of the Rh-based complexes is one of the most important conditions of their practical use. Therefore, the $acacRh(CO)_2$ --PEG-based system was tested in three successive experiments with intermediate separation of the reaction products from the catalyst if the catalytic aqueous layer was initially exposed to the reaction conditions in the synthesis-gas for 10 h without olefin. The results obtained are presented in Table 2.

It was found that preliminary exposure of the catalyst has no substantial effect on its activity, and the system

Table 1. Influence of the method of preparation of the acacRh $(CO)_2$ -PEG catalytic system on its properties during isobutene hydroformylation

Method of	Properties of catalytic system			
preparation	Starting complex		Aqueous layer	
	$r_0^* \cdot 10^3$	τ**	$r_0^* \cdot 10^3$	τ**
	/mol min ⁻¹	/h	/mol min ⁻¹	/h
Preliminary synthesis	0.6	3.0	0.5	3.5
in situ synthesis	1.0	4.5	0.9	6.5

* The rates of hydroformylation.

** Induction period.

Table 2. Hydroformylation of isobutene in the presence of the
acacRh(CO) ₂ -PEG catalytic system after its preliminary ex-
posure to hydroformylation conditions in the absence of olefin

Catalytic system	Recycle No.	$r_0^* \cdot 10^3$ /mol min ⁻¹	Induction period, t/h
Starting complex		0.50	3.5
Aqueous layer	1	0.47	3.7
	2	0.50	3.6

Note. Exposure conditions: T = 90 °C, p = 6.0 MPa, 10 h.

* The rates of hydroformylation.

retains its properties in two subsequent experiments (see Table 2).

Thus, the $acacRh(CO)_2$ -PEG-based catalytic system makes it possible to perform stable hydroformylation of isobutene with sufficiently high rates under mild conditions.

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