Hydroformylation of 1-hexene in the presence of rhodium complexes immobilized on polyorganosiloxanes

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It was demonstrated that the catalyst system based on acacRh(CO)$_2$ and polyorganosiloxanes exhibits high activity and stability in hydroformylation of 1-hexene. The effects of the nature of the oligomer, the ratio of oligomers, and the oligomer : rhodium ratio in the polymer on the synthesis and catalytic properties of the system were studied.

Key word: hydroformylation of olefins, rhodium catalyst, polyorganosiloxanes.

One important line of hydroformylation is the development of methods of heterogenization of rhodium carbonyl catalysts, which allow the use of medium-molecular and high-molecular olefins in this process.[1,2] When these catalysts are prepared, the stages of the synthesis of a polymer and immobilization of metallocomplexes can be combined. A procedure in which polymerization of monomers is initiated by a metal complex is most promising.[3]

In this work, we developed a method for the synthesis of catalysts for hydroformylation of 1-hexene based on acacRh(CO)$_2$ and polyorganosiloxanes and report the results of studies of the properties of these catalysts.

The polyaddition reaction used for preparing polyorganosiloxanes proceeds according to the following equation:

$$\equiv\mathrm{Si{-}H} + \mathrm{CH_2{=}CH{-}Si}\equiv \;\longrightarrow\; \equiv\mathrm{Si{-}CH_2{-}CH_2{-}Si}\equiv.$$

The acacRh(CO$_2$) complex, which initiated polyaddition, remained in the composition of the polymer.

The rhodium-containing polymer obtained was used as a catalyst in hydroformylation of 1-hexene. The effect of the concentration of the rhodium complex, the chemical composition, and the ratio of oligoorganosiloxanes on the catalytic properties of this system were studied.

Experimental

Rhodium-containing polyorganosiloxane (PS) catalysts (acacRh(CO)$_2$ · PS) were prepared from the corresponding compounds: (a) from oligovinylsiloxanes with methyl and phenyl substituents at the Si atom (the molecular weight was 8000—12000, and the bromine number was 37—49); (b) from oligohydrosiloxanes with methyl and phenyl substituents at the Si atom (the molecular weight was 8000—12000, and the content of active hydrogen was 0.35—0.43%); (c) from low-molecular organosiloxane rubber with terminal trivinylsiloxy groups (the molecular weight was 50000—70000, and the bromine number was 1.0—3.1), and (d) from the rhodium complex acacRh(CO)$_2$. Oligoorganosiloxanes were prepared according to the known procedure.[4] Low-molecular vinyl-containing rubber was prepared by equilibrium condensation of octamethylcyclotetrasiloxane with the calculated amount of vinyl-containing disiloxane as a reagent, which terminated the chain. The oligovinylsiloxane : oligohydrodesiloxane weight ratio was varied from 1 : 0.25 to 1 : 2. The acacRh(CO)$_2$ complex was prepared according to the known procedure.[5] The weight of the polymer charge was 8 g.

The catalysts were prepared by mixing siloxanes with the rhodium complex (in the presence of a solvent or without it) at room temperature followed by heating at 100—120 °C.

Hydroformylation of 1-hexene was carried out in a 0.25-L stainless-steel autoclave equipped with a stirrer. The reaction was performed in the batch mode at 120 °C and 6 MPa. The CO : H$_2$ molar ratio was 1 : 1. The reaction rate was monitored taking into account the amount of converted gas, which was measured from the decrease in the pressure in a calibrated vessel (gas was fed from this vessel to the autoclave as gas was consumed in the reaction mixture). The reaction rate was determined in the kinetic region of the process.

All experiments were carried out until conversion of substrate was 95%. Hydroformylation yielded *n*-heptanal and 2-methylhexanal. The selectivity of the reaction with respect to *n*-heptanal was 61%.

The reaction products were analyzed on a Crom-5 chromatograph (a 25-m capillary column packed with PEG 20 M; helium as the carrier gas; isothermal conditions; 100 °C). Carbon oxide and synthesis gas were prepared according to the known procedure.[1]

Results and Discussion

Heterogeneous catalysts have the advantage that they can be used many times without loss of their activity. In this connection, all catalysts were tested for stability in a series of successive runs with intermediate separation of the reaction products from the catalyst.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1155—1157, June, 1997.

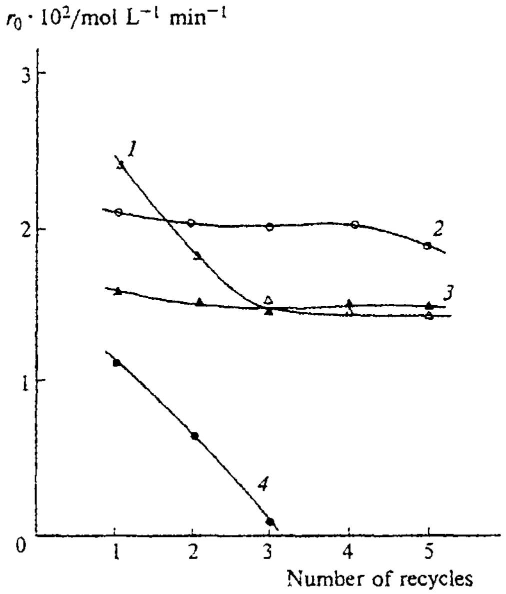

Fig. 1. Effect of the concentration of $acacRh(CO)_2$ in the phenyl-containing polymer on the catalytic properties of the system in hydroformylation of 1-hexene; $[acacRh(CO)_2] \cdot 10^{-3}$ (g of Rh/g of polyorganosiloxane) = 0.7 (*1*), 0.35 (*2*), 0.03 (*3*), and 0.02 (*4*) (T = 120 °C; p = 60 atm; CO : H_2 = 1 : 1; *p*-xylene as the solvent).

Preliminary studies of swelling of the polymers in various solvents demonstrated that the polymers exhibit high affinity for aromatic and aliphatic solvents. The weight of the polymer in *p*-xylene, hexane, and 1-hexene was almost doubled even in 1 h, whereas in aldehydes, the identical increase in the weight was attained in ~24 h. Polymers virtually did not swell in dioxane, water, and allyl alcohol.

We studied the effect of the concentration of $acacRh(CO)_2$ in the polymer on the synthesis and the catalytic properties of $acacRh(CO)_2 \cdot PS$. Phenyl-containing oligosiloxanes were used as components of the catalytic system. The results are given in Fig. 1. The reaction rate increased as the rhodium content of the polymer increased. However, durable hydroformylation of 1-hexene can be carried out only in the presence of catalytic systems in which the rhodium content is $(0.03-0.35) \cdot 10^{-3}$ g of Rh/g of the polymer. At higher concentrations of rhodium, polyaddition was accompanied by foaming, resulting in formation of nonhomogeneous samples. In this case, the polymer lost elasticity and became more friable. A decrease in the stability of the catalyst at a low rhodium content ($0.03 \cdot 10^{-3}$ g of Rh/g of polyorganosiloxane) is apparently associated with the fact that the polymer was partially converted to the gel state. Apparently, at low concentrations of rhodium, the polymer formed has a lower degree of cross-linking and becomes soluble. At the rhodium content of $>0.35 \cdot 10^{-3}$ g of Rh/g of polyorganosiloxane, the polymer lost its stability due to the polymer destruction and formation of rhodium complexes inactive in hydroformylation.[6]

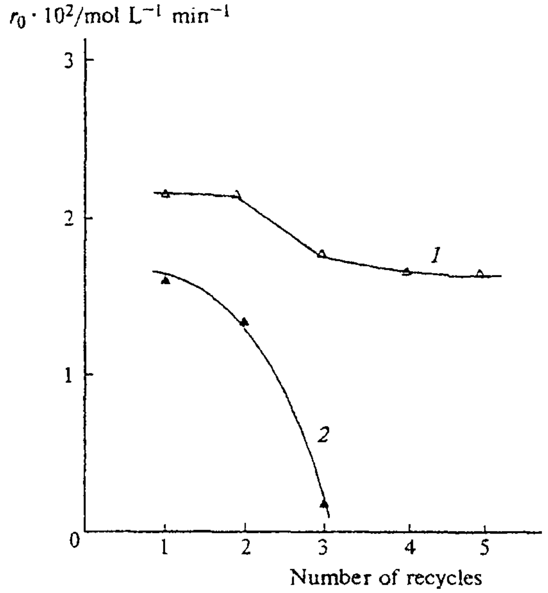

Fig. 2. Effect of the functional groups of organosiloxane on the catalytic properties of the system $acacRh(CO)_2 \cdot PS$ in hydroformylation of 1-hexene: *1*, phenyl groups; *2*, methyl groups (0.35 g of Rh/g of polyorganosiloxane; for the conditions see Fig. 1).

The catalytic properties of the system are substantially affected by the nature of the oligomer. As can be seen from Fig. 2, the use of oligomers with methyl substituents instead of phenyl-containing oligosiloxanes

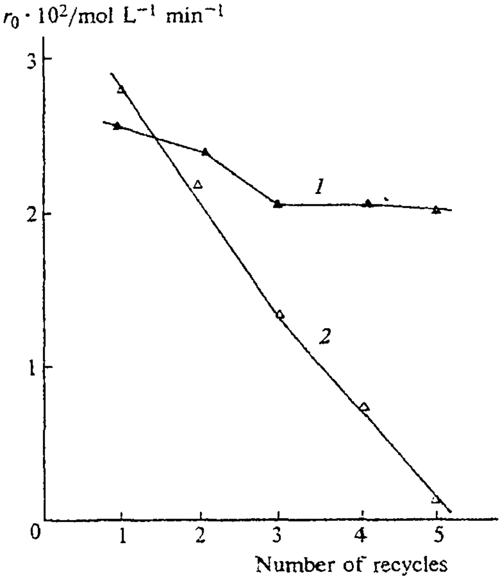

Fig. 3. Hydroformylation of 1-hexene in the presence of the catalyst applied to the bottom and walls of a reaction vessel as a film (*1*) and prepared in a thermostat (*2*) (for the conditions see Figs. 1 and 2).

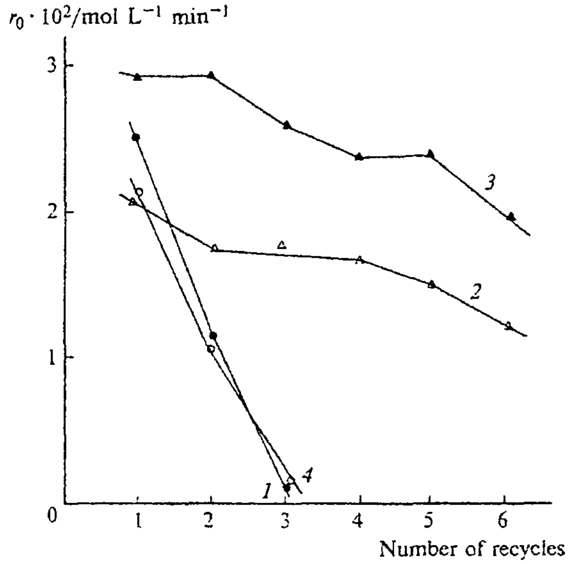

Fig. 4. Effect of the oligovinylsiloxane : oligohydridesiloxane weight ratio in the polymer on the catalytic properties of the system in hydroformylation of 1-hexene: 1 : 0.25 (*1*), 1 : 1 (*2*), 1 : 2 (*3*), and 1 : 4 (*4*) (for the conditions see Figs. 1 and 2).

resulted in a decrease in the activity and loss of stability. Apparently, this is associated with the fact that when phenyl substituents were replaced by methyl substituents, more rigid and friable polymers were formed with a lower degree of swelling in organic solvents. A change in the physical properties of the polymer is reflected in the catalytic properties of the system. A low degree of swelling results in a decrease in the activity, and friability leads to mechanical destruction of the catalyst in the course of the reaction and deactivation of the rhodium complexes.

With the aim of decreasing mechanical destruction of the catalyst, the polymer was applied to the bottom and walls of the reaction vessel as a film. As can be seen from Fig. 3, this method of preparation of the catalyst allows its reuse without loss in the activity.

Polyaddition of oligosiloxanes can be carried out with the weight ratio of oligomers varied over a wide range. However, a deficiency or an excess of oligohydridesiloxane has a substantial effect on the physical properties of the polymer obtained. As can be seen from Fig. 4, the best results were obtained when we used catalytic systems based on polymers with oligovinylsiloxane : oligohydridesiloxane weight ratios in the range from 1 : 1 to 1 : 2. When the vinyl oligomer content was increased, the catalyst, which was noticeably soluble in the reaction mixture at high temperature, formed. In the case of an excess of the hydride-containing oligomer, the polymer became friable, which also impaired the stability of the catalyst system.

The catalyst with the weight ratio of vinyl and hydride components of 1 : 2 was tested in the continuos mode. Hydroformylation of 1-hexene was carried out in a flow setup. The catalyst worked without loss in the activity over the entire period of the experiment (T = 120 °C, p = 60 atm, CO : H_2 = 1 : 1, ω_g = 1000 h^{-1}, ω_l = 3 h^{-1}, the time of the experiment was 100 h). Atomic absorption analysis demonstrated that rhodium was absent in the reaction products.

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Received October 25, 1996;
in revised form January 14, 1997