Modification of rhodium carbonyl catalysts for hydroformylation of 2-butenes by organophosphorus ligands

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The influence of the nature of the organophosphorus ligand and the P/Rh molar ratio on the catalytic properties of rhodium carbonyl complexes in hydroformylation of 2-butenes was studied. The difference between phosphine and phosphite ligands during the formation of highly selective catalytic complexes was found. It was supposed that a decrease in the selectivity with respect to 2-methylbutanal is due to the isomerization of olefins under conditions of a decrease in the competitive capability of CO for coordination sites (the high P/Rh ratio, a decrease in the total pressure of the synthesis-gas).

Key words: hydroformylation, rhodium catalyst, organophosphorus compounds.

The efficiency of rhodium-based catalysts increases substantially when they are modified by organophosphorus ligands. The characteristics of modification of rhodium complexes by organophosphorus ligands have mainly been studied for the hydroformylation of α-olefins.[1—3] Data for olefins with an internal double bond are virtually lacking.

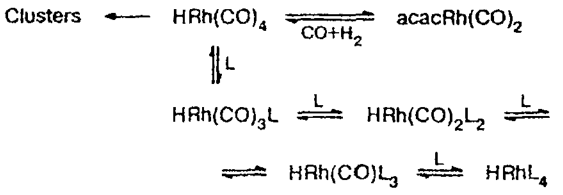
In this work, we studied the effect of the nature of the organophosphorus compound and the P/Rh ratio on the catalytic properties of rhodium carbonyl complexes in hydroformylation of 2-butenes. Triphenylphosphine, tributylphosphine, triphenyl phosphite, tributyl phosphite, and etriol phosphite, the main representatives of the spectrochemical series of organophosphorus ligands, were used as organophosphorus ligands.

Experimental

Hydroformylation of 2-butenes was carried out in a 0.25 L autoclave of stainless steel with a stirring device at $T = 90$ °C, $p = 2—6$ MPa, and rhodium concentration ([Rh]) of $3.0 \cdot 10^{-4}$ g-at. L^{-1}. The reaction rates were monitored by the amount of consumed synthesis-gas (SG), which was measured by the pressure drop in the calibrated vessel (from which the gas was supplied to the autoclave while being consumed) and determined as the ratio of the number of SG moles to time (min). The reaction products were analyzed on a Chrom-5 chromatograph (a capillary column 25 m long, PEG-20M, helium as the carrier gas, 110 °C). Two isomers are formed in the hydroformylation of 2-butenes: *n*-pentanal and 2-methylbutanal (2-MB). The selectivity with respect to 2-MB was determined as the ratio of the amount of 2-MB to the total amount of the aldehydes formed. Carbon monoxide was obtained by dehydration of formic acid with sulfuric acid. Synthesis-gas was obtained by mixing of electrolytic H_2 and CO and purified with Cu/SiO_2 catalyst and then with Cr_2O_3/SiO_2 sorbent to a residual content of O_2 of 10^{-6}%. The following reagents were used: $acacRh(CO)_2$ prepared according to the procedure described previously,[4] triphenyl phosphite with b.p. 183—184 °C (1 Torr), $R_f = 0.9$ (Silufol UV-254, benzene—dioxane (3 : 1)),[5] and etriol phosphite, b.p. 55—56 °C, $R_f = 0.37$ (Silufol UV-254, benzene).[6] The $acacRh(CO)_2 + n$ L systems were formed *in situ* in *p*-xylene at 20 °C. 2-Butenes were obtained by disproportionation of propene (composition, wt.%: C_3H_8, 0.2; C_4H_8, 1—0.7; *trans*-C_4H_8-2, 53.63; *cis*-C_4H_8-2, 45.64).

Results and Discussion

The effect of the P/Rh molar ratio on the catalytic properties of rhodium carbonyl complexes was studied for the whole series of organophosphorus ligands within the range of the P/Rh ratios from 1 to 50. For all organophosphorus ligands, the dependences of the initial rates on their concentrations are extreme. The presence of a maximum is related to the fact that in the reaction zone, complexes with different degrees of substitution are in equilibrium, which depends on the concentration of the ligand and its nature.



$$\text{Clusters} \longleftarrow HRh(CO)_4 \underset{CO+H_2}{\rightleftharpoons} acacRh(CO)_2$$
$$HRh(CO)_4 \overset{L}{\rightleftharpoons} HRh(CO)_3L \overset{L}{\rightleftharpoons} HRh(CO)_2L_2 \overset{L}{\rightleftharpoons} HRh(CO)L_3 \overset{L}{\rightleftharpoons} HRhL_4$$

An increase in the degree of substitution is accompanied by strengthening of the M—CO bond, which decreases the catalytic activity. At a low concentration of the ligand, the equilibrium is shifted toward the formation of unmodified complexes prone to aggregation re-

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sulting in inactive clusters.[7] Under the conditions where the rates of 2-butene hydroformylation reach the highest value, the concentration of the catalytically active centers is maximum. The results for triphenylphosphine, triphenyl phosphite, and etriol phosphite, the most characteristic representatives of their class, are presented in Fig. 1. For each ligand, the highest rates are achieved at different P/Rh ratios. For example, the triphenyl phosphite-modified rhodium carbonyl complex (see Fig. 1) exhibits the highest activity at P/Rh = 2. In the case of etriol phosphite and triphenylphosphine, the maximum is less pronounced and corresponds to the ratios P/Rh = 6 for $P(OCH_2)_3CEt$ and P/Rh = 3 for PPh_3.

For all the ligands used, the selectivity of the catalyst with respect to 2-methylbutanal increases monotonically and reaches ~100%. For each organophosphorus compound, a certain P/Rh ratio corresponds to the highest selectivity. The coordination environment of rhodium corresponding to the highest selectivity is created at some "threshold" concentration of the ligand (P/Rh), which is first determined by its capability of competing with CO. The results obtained show the interrelation of the nature of the organophosphorus ligand and the catalytic properties of the complexes based on it.

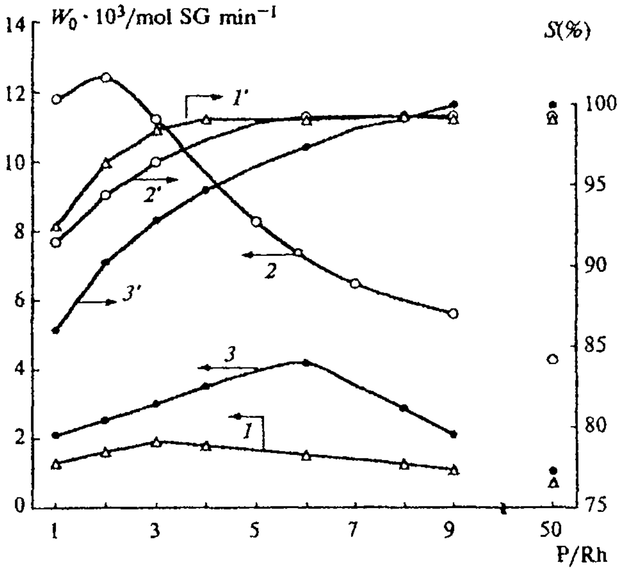

Fig. 1. Effect of the phosphorus/rhodium molar ratio (P/Rh) on the activity (W_0) (*1—3*) and selectivity with respect to 2-methylbutanal (*S*) (*1'—3'*) of the rhodium carbonyl catalyst modified by triphenylphosphine (*1, 1'*), triphenyl phosphite (*2, 2'*), and etriol phosphite (*3, 3'*) in hydroformylation of 2-butenes (p = 6 MPa).

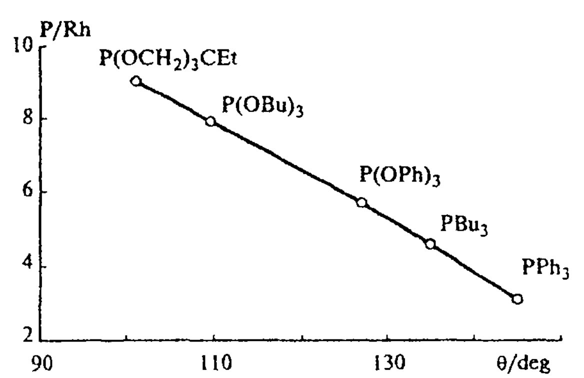

Fig. 2. Dependence of the P/Rh molar ratio necessary for the achievement of the limiting selectivity of the catalyst with respect to 2-methylbutanal on the value of the cone angle of the P-ligand (θ).

The steric and electronic factors of the phosphorus ligand are reflected most completely by its cone angle (θ),[8] which determines the ability of the ligand to substitute CO and, hence, the selectivity of the catalytic complex. As can be seen in Fig. 2, in the case of phosphites, the highest selectivity is achieved at a higher P/Rh ratio than that for the phosphine systems. This can be explained by the fact that phosphites are characterized by a lower value of the cone angle than phosphines and are closer in properties to the carbonyl group. Due to this, higher concentrations of phosphites are necessary under hydroformylation conditions (p = 6 MPa) for shifting the equilibrium toward the selective phosphorylated catalytic center.

A decrease in the pressure of the synthesis-gas favors the formation of phosphorylated complexes, and the selectivity for the phosphite systems should reach the limiting value at a lower P/Rh ratio. In the hydroformylation of 2-butenes in the presence of the etriol phosphite-modified catalyst, as the pressure decreases to 2 MPa, the selectivity with respect to 2-methylbutanal decreases substantially and the content of *n*-aldehydes increases (Fig. 3). Since the formation of *n*-aldehydes is mainly due to the presence of *n*-alkyl complexes, the synthesis of aldehydes with the straight

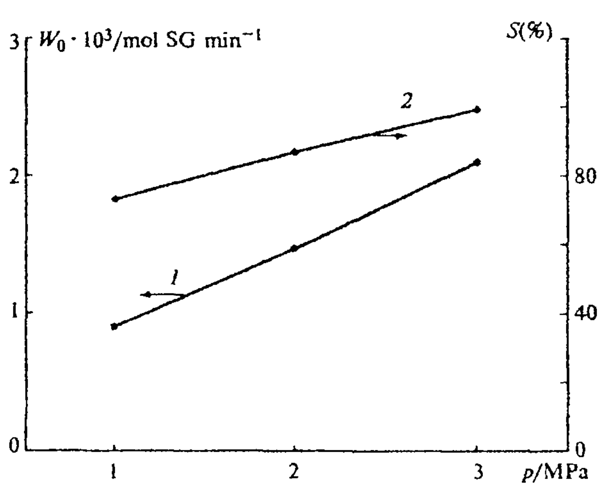

Fig. 3. Effect of the total pressure (p) on the activity (W_0) (*1*) and selectivity with respect to 2-methylbutanal (*S*) (*2*) of the catalyst modified by etriol phosphite (P/Rh = 9) in hydroformylation of 2-butenes.

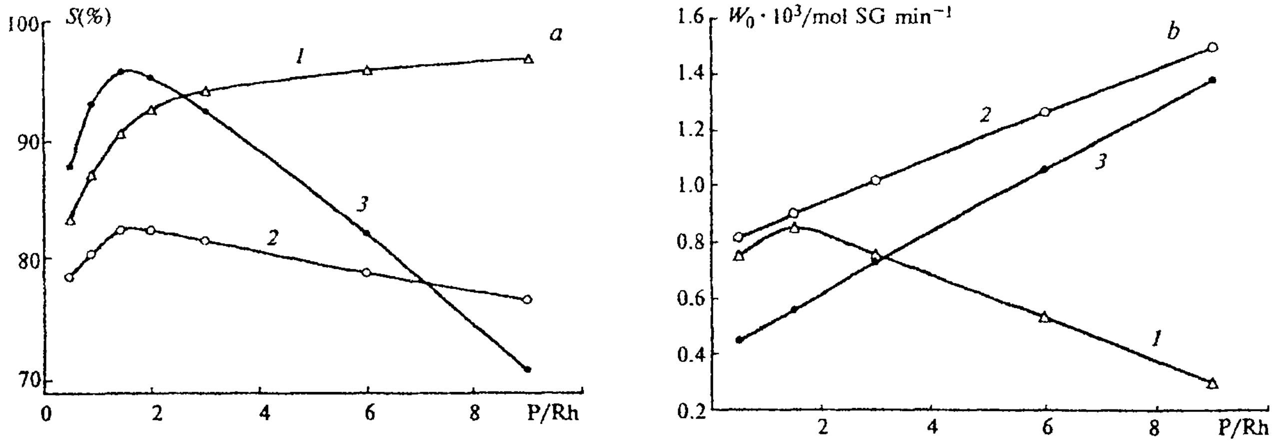

Fig. 4. Influence of the P/Rh molar ratio on the selectivity with respect to 2-methylbutanal (*S*) (*a*) and activity (W_0) (*b*) of the catalyst in hydroformylation of 2-butenes for triphenylphosphine (*1*), triphenyl phosphite (*2*), and etriol phosphite (*3*) (p = 2.0 MPa).

chain in the case of β-olefin (unlike α-olefins) requires the stage of its isomerization.

Isomerization of β-olefins is favored by high steric hindrances at the Rh atom, because under these conditions, highly phosphorylated complexes $HRhL_4$ can be formed due to a small cone angle of the ligand and a high P/Rh ratio. The isomerizing capability of these complexes has previously been observed.[9] The completely phosphorylated rhodium complex responsible for isomerization cannot be obtained at high pressures (6 MPa) even at a ratio of P/Rh = 50 (see Fig. 1).

The effect of the ligand concentration on the selectivity of the catalytic system of 2-butene hydroformylation was studied at $p = 2$ MPa (CO : H_2 = 1 : 1). As can be seen in Fig. 4, *a*, in the case of phosphites, this dependence is extreme. For the phosphine system, as the P/Rh molar ratio increases, the selectivity with respect to 2-methylbutanal increases, reaching the highest value at P/Rh = 6. Further increase in the concentration of PPh_3 does not result in a change in the selectivity.

Thus, under the conditions where the competition of CO for coordination sites is weakened, different situations can occur, depending on the nature of the ligand. In the case of phosphites with a small cone angle, as the concentration of the ligand increases, highly phosphorylated complexes are easily formed, which favor the isomerization of α-olefins and affecting the distribution of hydroformylation products. This fact is indirectly confirmed by an increase in the hydroformylation rate with an increase in the concentration of phosphites (Fig. 4, *b*), since α-butenes, whose hydroformylation occurs with higher rates, are accumulated in the reaction mixture due to isomerization. In the case of phosphine (see Fig. 4, *a*) characterized by a large cone angle, no complexes with a high degree of substitution are formed even at high concentrations of the ligand and no steric hindrances favoring the olefin isomerization appear. The decrease in the reaction rates at P/Rh > 2 is most likely related to reactions of formation of rhodiumphosphido clusters inactive in hydroformylation and products of orthometallation of the phosphine ligand.[10] These reactions proceed with a higher intensity as the CO pressure decreases.

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