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Carbonylation of methyl acetate in the presence of polymeric rhodium-containing catalysts

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New catalytic systems based on $RhCl_3$ and polymeric nitrogen- and oxygen-containing supports were proposed for the carbonylation of methyl acetate to acetic anhydride. The catalytic systems possess a high activity typical of homogeneous catalysts. The high activity is retained upon the repeated use of the catalyst separated from the reaction products. The nitrogen-containing polymers of the chitosan type serve as cocatalysts. In their presence, the induction period disappears, and the catalytically active species are stabilized, thus enabling the replacement of expensive LiI for cheaper salts of this metal.

Key words: carbonylation, methyl acetate, rhodium-containing catalysts.

Two main commercial processes for acetic anhydride production are presently available[1,2]: from acetic acid through ketene at 750 °C and from acetaldehyde by its oxidation. Both processes are uneconomical, which leads to a high cost of acetic anhydride. Among alternative methods for its production, the Eastman Co. process is of most interest, *viz.*, AcOMe homogeneous carbonylation in the presence of $RhCl_3$.[3] Carbonylation of AcOMe by this method occurs in the presence of MeI and anhydrous LiI under a gas mixture pressure of 5 MPa (95% CO + 5% H_2) and at 190 °C.

The purpose of this work is to develop a new variant of AcOMe carbonylation to Ac_2O in the presence of Rh-containing polymeric catalytic systems. Natural (chitosan, chitin, and polyglucin) and synthetic polymers (styrene copolymers containing pyrrolidinopyridine (STPP) and pyridylmaleimide (STPM) groups) were used as ligands (Table 1).

Experimental

Carbonylation of AcOMe was conducted at 190 °C and a pressure of 5 MPa in a glass reactor placed in a stainless steel autoclave. The reaction mixture was magnetically stirred. The reaction rate was monitored by the amount of the absorbed gas (95 vol.% CO + 5 vol.% H_2), which was measured from the pressure drop in a calibrated vessel, from which the gas was supplied to the reactor with consuming, and determined as a ratio of the number of moles of the gas mixture to the time (min) and volume of the catalytic solution.

The catalytic system was prepared directly in the reactor from $RhCl_3 \cdot 4H_2O$ (0.038 mmol), macroligand (chitosan, chitin, polyglucin, and STPM or STPP) at different L : Rh ratios (L is the structural unit of the macroligand) (Table 2), LiI (0.006 mol), MeI (1 mL), AcOH (4 mL), and AcOMe (14.5 mL). The temperature was risen to 190 °C and the pressure was increased to 5 MPa.

Reaction products were analyzed on a Chrom-5 chromatograph (packed column 2.5 m, Porapak Q, flame-ionization detector, nitrogen as carrier gas, T = 150 °C). According to the GLC data, Ac_2O is the only reaction product. Conversion of AcOMe was determined as the difference between the concentrations of AcOMe in the initial reaction mixture and reaction products.

Stability of the catalytic system was estimated from the reaction rate upon the catalyst recycle after the removal of the reaction products.

The content of Rh in the polymer before and after the reaction was determined by atomic-absorption spectrophotometry.

Results and Discussion

The study of the influence of polymeric supports (chitosan and polyglucin) containing various heteroatoms on the catalytic properties of $RhCl_3$ (Fig. 1) showed that in the presence of $RhCl_3$ without a macroligand the reaction occurs with a low rate and a considerable induction period. The reaction is ceased after 4 h at an AcOMe conversion of ~36%. When polyglucin is used as a polymeric support, the reaction occurs similarly, *i.e.*, the induction period is observed, and the catalytic system also exhibits low activity. A different situation is observed in the presence of the $RhCl_3$—chitosan system. Although the reaction rate increases insignificantly, the induction period disappears, and after 4 h the reaction rate remains virtually unchanged. Thus, chitosan not only accelerates the formation of the catalytically active Rh speciees but also stabilizes them. It is known[4] that LiI is needed to

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Table 1. Structure and molecular weight (M) of macroligands

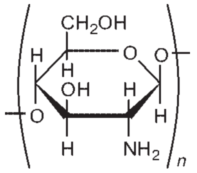
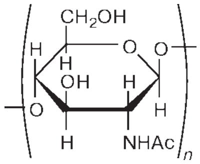
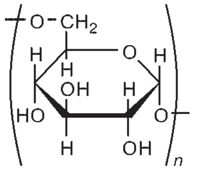
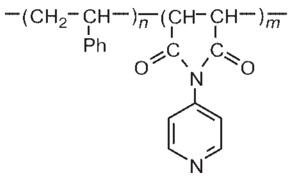
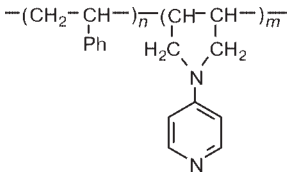
Macroligand		M
	Natural ligands	
Chitosan		60000
Chitin		60000
Polyglucin		60000
	Synthetic ligands	
STPM		70000
STPP		70000

Table 2. Influence of $RhCl_3$ modified by various macroligands on the initial carbonylation rate of AcOMe (r_0)

Macroligand	Ratio N : Rh	$r_0 \cdot 10^2$/mol L^{-1} min^{-1}	
		Fresh catalyst	Catalyst after removal of products
STPP	16	3.5	2.5
STPM	16	1.8	1.0
Chitin	24	2.0	—
Chitosan	15	3.2	—
Chitosan	30	3.3	—
Chitosan	60	3.3	—
$RhCl_3$	—	3.5	—

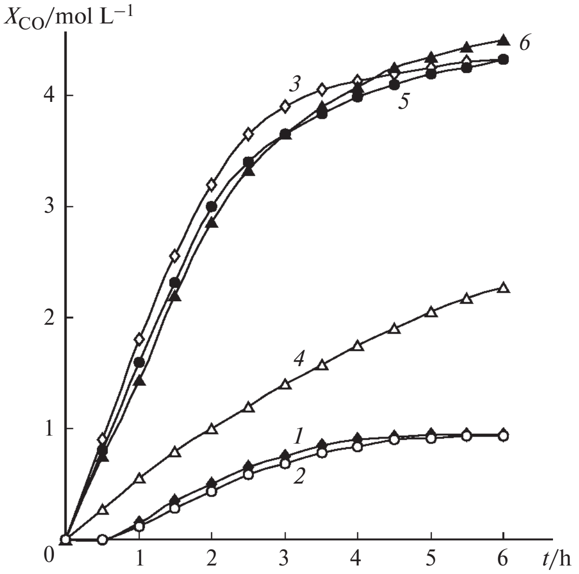


Fig. 1. Absorption of CO (X_{CO}) as a function of the duration (*t*) of AcOMe carbonylation (190 °C, 5 MPa) in the presence of various catalytic systems: $RhCl_3 \cdot 4H_2O$ (*1*); $RhCl_3$—polyglucin (*2*), $RhCl_3$—LiI (*3*), $RhCl_3$—chitosan (*4*), $RhCl_3$—LiI—polyglucin (*5*), and $RhCl_3$—LiI—chitosan (*6*).

increase the rate of AcOMe carbonylation in the presence of $RhCl_3$. LiI performs several functions: first, it decreases the induction period of the reaction due to the faster transformation of the inactive Rh^{III} into active Rh^{I}; second, changes the reaction route due to which the liberation of MeI is strongly accelerated (oxidative addition of MeI is the rate-determining stage of the process) and virtually excludes the formation of HI, which favors the transformation of the catalytically active $Rh(CO)_2I_2^-$ complexes into inactive $Rh(CO)_2I_4^-$.

Indeed, when LiI is added to both $RhCl_3$ and the $RhCl_3$—polyglucin system, the induction period disappears, the reaction rate significantly increases, and after 6 h the conversion of AcOMe reaches ~90%. In the presence of the $RhCl_3$—chitosan—LiI system, the reaction rate also increases, and after 6 h the conversion of AcOMe becomes >95% (see Fig. 1).

Thus, chitosan accelerates the transition of the inactive Rh form to the active species, due to which the induction period disappears, and stabilizes the catalytically active species.

The Rh-catalyst is deactivated mainly due to the accumulation of I_2, formed by the thermal decomposition of AcI, and HI, which is the product of the reaction of AcI with AcOH. Both deactivating agents (I_2 and HI) favor[5] the transition of active species to inactive. Unlike polyglucin, chitosan and other N-containing polymers (STPP and STPM) capable of binding HI and AcI accumulated in the system to form quaternary ammonium

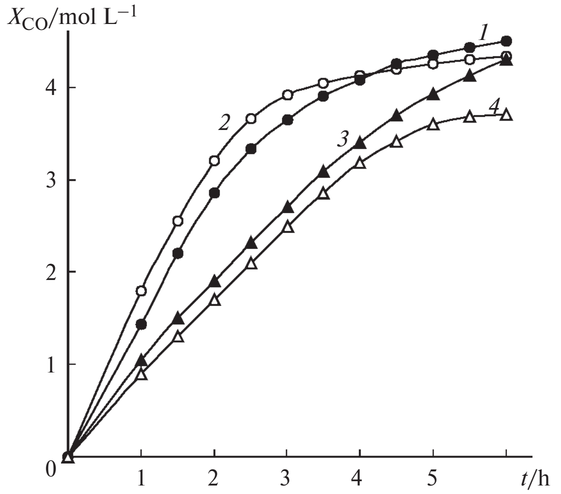


Fig. 2. Absorption of CO (X_{CO}) as a function of the duration (*t*) AcOMe carbonylation (190 °C, 5 MPa) in the presence of various catalytic systems: $RhCl_3$—LiI—chitosan—MeI (*1*), $RhCl_3$—LiI—MeI (*2*), $RhCl_3$—LiI—chitosan—HI (*3*), and $RhCl_3$—LiI—HI (*4*).

salts,[6] preventing the thermal decomposition of the latter to evolve I_2.

The specificity of the mutual influence of HI and chitosan in this reaction was studied. The replacement of MeI by HI decreases considerably the reaction rate in the presence of $RhCl_3$ and the $RhCl_3$—chitosan system (Fig. 2). In both cases, the initial rates are virtually the same; however, in the absence of chitosan, after 4 h the catalyst activity decreases, and after 6 h the reaction is entirely ceased, and the conversion of AcOMe does not exceed 80%. By contrast, in the presence of chitosan, the reaction rate remains almost unchanged, and after 6 h the conversion of AcOMe becomes >90%. These data confirm the fact that chitosan aligns the deactivating role of HI by the formation of quaternary ammonium salts.

The influence of various Li salts on the catalytic properties of the Rh-containing catalysts was studied. As can be seen in Fig. 3, *a*, the replacement of LiI by Li_2CO_3 or LiOAc in the system without chitosan decreases the reaction rate. This can be attributed to a deficient of the I^- ions, which decreases the rate of MeI formation in the reaction of LiI with AcOMe. In the case of Li_2CO_3, water and HI, which deactivate the Rh catalyst, can also be formed in the system.

Quite different situation is observed in the case of the polymeric catalyst (Fig. 3, *b*). The reaction rates are almost equal when all three salts are used. The accelerating function of chitosan is possibly carried out through its capability of alkylating MeI at the N atom. The coordination of the alkylated macroligand with the catalytically active $Rh(CO)_2I_2^-$ complex favors the oxidative addition of MeI to the Rh atom.

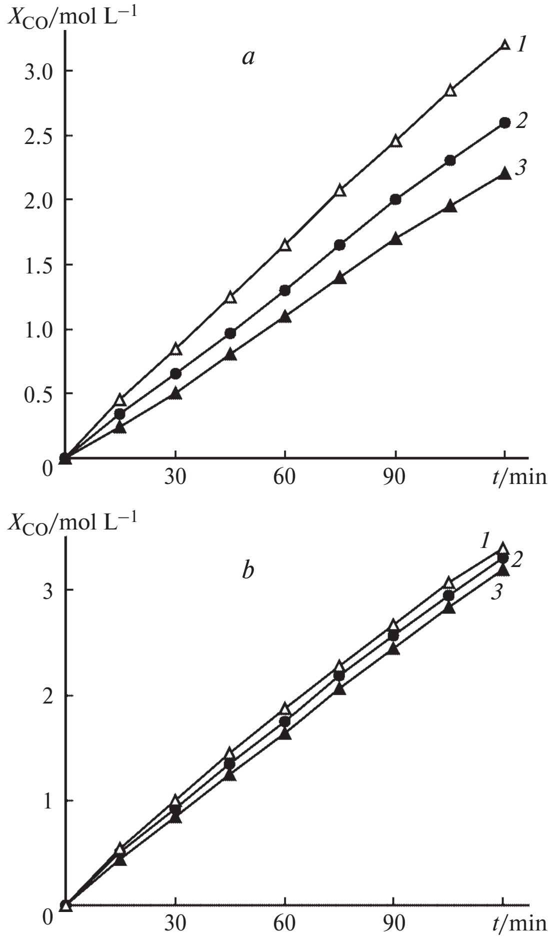


Fig. 3. Influence of various Li salts on the activity of the $RhCl_3 \cdot 4H_2O$ (*a*) и $RhCl_3$—chitosan systems (*b*): LiI (*1*), AcOLi (*2*), and Li_2CO_3 (*3*).

Thus, the use of chitosan as a support allows cheaper Li salts to be introduced as a promoter.

The study of the influence of various nitrogen-containing polymers and the molar N : Rh ratio for chitosan on the initial carbonylation rate (r_0) (see Table 2) showed that only STPP has the same high activity as chitosan, which is not inferior to that of the homogeneous $RhCl_3$—LiI catalytic system. In addition, in the case of chitosan, the carbonylation rate is independent of the N : Rh molar ratio in an interval from 15 to 60. After the reaction products were separated from the catalyst and the latter was repeatedly applied, its activity decreased. This is associated with a loss of some portion of the polymeric catalyst when STPP or STPM is used as the support due to partial dissolution in the liquid phase. In the case of chitin and chitosan, this is due to a loss of Rh (by more than an order of magnitude), which was confirmed by atomic-absorption spectroscopy.

Another variant of recycle of the catalytic system was studied for chitosan. The reaction products were sepa-

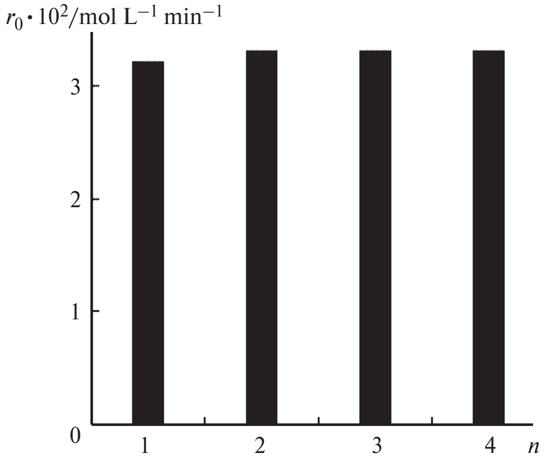


Fig. 4. Influence of the number of catalytic cycles (n) on the initial rate of AcOMe carbonylation (r_0) ($RhCl_3$—LiI—chitosan system, 190 °C, 5 MPa) in a series of successive experiments with the intermediate separation of the reaction products from the catalyst.

rated from the catalyst by distillation, the vat residue containing the Rh complex, polymer, and LiI was returned to the reactor, and AcOMe carbonylation was repeated. As can be seen in Fig. 4, for this variant of recycle, the activity of the catalytic system is retained and even somewhat increases in subsequent experiments. This indicates that chitosan can retain the alkylated and acylated forms and coordinate with active anionic Rh complexes stabilizing them.

The data obtained in this work show that the nitrogen-containing polymers (*viz.*, chitosan and STPP) enhance the performance of the Rh catalyst in AcOMe carbonylation due to an increase in the rate of formation of the active species and their stabilization. In addition, these polymers allow the replacement of expensive LiI for cheaper Li salts.

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