1858 *Russian Chemical Bulletin, International Edition, Vol. 60, No. 9, pp. 1858—1861, September, 2011*

Effect of protic agents on the catalytic activity of supported palladium catalysts in the copolymerization of ethylene with carbon monoxide

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The influence of the addition of different amounts of MeOH, H_2O, and HCOOH on the activity of supported palladium catalyst in the copolymerization of CO with ethylene and the kinetic regularities of this reaction were studied for the first time. The maximum yield of the copolymer is attained when MeOH and H_2O or HCOOH and H_2O are simultaneously introduced into the reaction medium (toluene). The results obtained are consistent with the concepts about the role of protic agents in the formation of active intermediates and polymer molecules in the copolymerization of CO with ethylene in the presence of the homogeneous catalytic systems.

Key words: polyketones, copolymerization, supported catalyst, ethylene, carbon monoxide, methanol, water, formic acid.

The copolymerization of CO with olefins with the formation of strictly alternating copolymer (polyketone, PK) occurs in the presence of ionic palladium complexes $[PdL_2X_2]$ (L_2 is a bidentate ligand, and X is a weakly coordinated anion) in protic media (MeOH, H_2O). The reaction is often carried out in a mixture of polar solvents (for example, CH_2Cl_2, THF, $MeNO_2$) and protic agents. The latter participate in all steps of the catalytic cycle resulting in the formation of the polymer chain. The main steps of the alternating CO/olefin copolymer formation were described in detail in several reviews.[1—4] It is considered that MeOH plays an important role in the production of active intermediates $PdL_2(OMe)^+$ (**1a**) and PdL_2H^+ (**1b**) and in the reaction of polymer chain termination and in the regeneration of active sites. These functions can also be performed by other protic agents as well. It is known, for instance, that the copolymerization of CO with olefins can be carried out in the presence of H_2O.[4]

There are few experimental data on the effect of protic agents on the activity of the palladium catalysts and the yield of copolymer in homogeneous catalytic systems. The copolymerization of CO with propylene in CH_2Cl_2 on the catalyst $[Pd(dppp)(NCCH_3)_2](BF_4)_2$ (dppp is 1,3-bis(diphenylphosphino)propane) occurs in the presence of both methanol and water without methanol.[4] The effect of the content of water on the activity of the palladium catalysts was studied for a reaction in a mixture of acetic or formic acid with water.[5,6] It was suggested that the presence of water increases the concentration of hydride intermediates **1b**. These can be produced particularly by reaction (1) similar to water-gas shift reaction.

$$\text{Pd—C(O)OH}^+ \longrightarrow \text{Pd—H}^+ + \text{CO}_2 \qquad (1)$$

The concentration of the hydride complexes also increases upon the addition of acids (*e.g.*, TsOH, TfOH, and HBF_4) to the reaction mixture.[1—4]

The data on the influence of the protic agents (MeOH, H_2O, and acids) on the activity of the ionic palladium catalysts in olefin copolymerization with CO were obtained for the homogeneous catalytic systems. Earlier we have shown[7] for the first time that olefin/CO copolymerization occurs efficiently in the presence of the supported palladium catalysts in weakly polar media (heptane, toluene), which are not of common use for olefin/CO copolymerization on the ionic palladium complexes. Under these conditions, the strictly alternating copolymer of CO with ethylene was obtained, which was similar to the copolymer formed under the homogeneous conditions with the ionic palladium complexes.[7] The purpose of the present work is the study of the change in the activity of the supported catalysts and the yield of PK upon the addition of various amounts of protic agents (MeOH, H_2O, and HCOOH) into the reaction medium.

Experimental

Materials. Samples of MeOH (reagent grade, 0.5 wt.% H_2O), TsOH monohydrate (reagent grade), HCOOH (pure), toluene

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1825—1828, September, 2011.

(special purity grade), CO (98 vol.%, OAO Redkinskii Experimental Plant, Russia), and ethylene (99.9 vol.%, OAO Nizhnekamskneftekhim, Russia) were used as received. Toluene contained 0.045 wt.% water.[8] The purity of monomers was monitored chromatographically on an LKhM-80 gas chromatograph with a Porapak Q column, and the purity of toluene was checked on a Gilson liquid chromatograph. The water content in methanol was determined using the Fischer method.

The supported catalyst (Cat) $[Pd(dppp)(TsO)_2]$/Poly (Poly is polymer support PK) was synthesized according to a previously described procedure.[7] The Pd content in the catalyst was $(2.2—2.5) \cdot 10^{-4}$ mol g_{Cat}^{-1}.

Copolymerization of CO with ethylene. The alternating copolymerization of CO with ethylene was carried out in toluene in the presence of Cat and various protic agents (MeOH, H_2O, acids TsOH and HCOOH). The temperature of the reaction was 90 °C, and the liquid phase volume was 66.4—70.0 mL. A constant pressure of 4 MPa was maintained during the reaction. This pressure was created in the reactor by feeding a mixture of CO with ethylene, $n(CO)/n(C_2H_4) = 1$ (n is the amount of the substance, mol). The supported catalyst as a powder was introduced into the reactor in glass ampules or was put in argon. The catalyst weight was 0.08—0.12 g. The time dependence of the polyketone yield was studied by measuring the pressure drop of a CO—ethylene mixture in a volumetric cylinder.[7]

The synthesized copolymer of CO with ethylene was analyzed by recording the IR reflectance spectra on a Perkin—Elmer FT-IR instrument. The IR spectra of the strictly alternating CO/ethylene copolymer are characteristic and have an intense band corresponding to the carbonyl group vibrations at 1693 cm^{-1} and a set of bands attributed to the stretching (in the region of 2913 cm^{-1}) and bending (at 812, 1335, and 1408 cm^{-1}) vibrations of the CH_2 groups. The detailed description of the IR spectra of the strictly alternating CO copolymer with ethylene is available from the earlier published article.[7]

Results and Discussion

It has earlier been shown[9] that for the catalysts immobilized on the polymer support the maximum yield of copolymer (Y) per 1 g of the support per 1 h is achieved at a Pd content of $2 \cdot 10^{-4}$ mol g_{Cat}^{-1}. In order to obtain the same specific yield of PK, in this work we used the supported catalysts with the Pd content from $2.2 \cdot 10^{-4}$ to $2.5 \cdot 10^{-4}$ mol g_{Cat}^{-1}.

The reactions of polymer chain termination can involve MeOH or H_2O. When studying the formation of the CO/ethylene copolymers in a toluene medium in the presence of Cat, we showed that, with all other conditions equal, the rate of formation of the product in the presence of small additives of H_2O is 10 times lower than that observed with MeOH.[7] In this work we studied the change in the specific yield of the copolymer for the case of simultaneous addition of these agents. The data illustrating the change in the specific yield of the CO/ethylene copolymer in the presence of Cat upon the addition of MeOH and H_2O are presented in Tables 1 and 2.

Table 1. Influence of the MeOH content in the reaction mixture on the yield of polyketone

Entry	V_{MeOH}/mL	$n(MeOH)/n(Pd)$	Y*/g g_{Cat}^{-1}
1	3	3000	45.6
2	4	4000	56.5
3	5	5800	64.8
4	7	7600	62.3

* TsOH ($n(TsOH)/n(Pd) = 4$) was introduced into the reaction mixture. The reaction time was 2 h.

The specific yield of PK increases with an increase in the amount of MeOH and attains the maximum value when 5 mL of MeOH is added ($n(MeOH)/n(Pd) = 5800$), while no increase in the copolymer yield is observed at a higher concentration of the additive. This pattern of dependence is related, most likely, to the fact that MeOH is necessary in fairly large amounts as an agent for polymer chain termination. Its optimum content for the formation of an active catalytic system can vary with a change in the specific conditions of the synthesis (nature of the reaction medium, reactor volume, reaction temperature, *etc.*). An additional introduction of water into the reaction medium up to a volume of 0.5 mL ($n(H_2O)/n(Pd) = 1600$) is accompanied by an increase in the PK yield. Thus, the simultaneous presence of these protic agents provides the maximum activity of the supported catalysts when the reaction is carried out in toluene. The PK yield decreases sharply with a further increase in the amount of H_2O (2 mL and more). Similar data were obtained for the copolymerization of CO with propylene in the presence of the homogeneous catalytic system in CH_2Cl_2 with additives of H_2O without MeOH. It turned out that the maximum activity of the catalyst was observed upon the addition of small amounts of water to the reaction medium (0.1—0.2 mL), whereas the addition of 2 mL of water decreases the activity of the system.[4] An increased rate of copolymerization induced by the addition of small amounts of water is attributed to an increase in the concentration of the active hydride complexes.[1—6] However, the introduction of considerable amounts of water is accompanied by the reduc-

Table 2. Influence of the H_2O content in the reaction mixture on the yield of polyketone

Entry	V_{H_2O}/mL	$n(H_2O)/n(Pd)$	Y*/g g_{Cat}^{-1}
1	0.0	0	64.8
2	0.2	400	70.7
3	0.5	1600	88.0
4	1.0	2200	56.7
5	2.0	4700	1.0

* TsOH ($n(TsOH)/n(Pd) = 4$) and 5 mL of MeOH were introduced into the reaction mixture. The reaction time was 2 h.

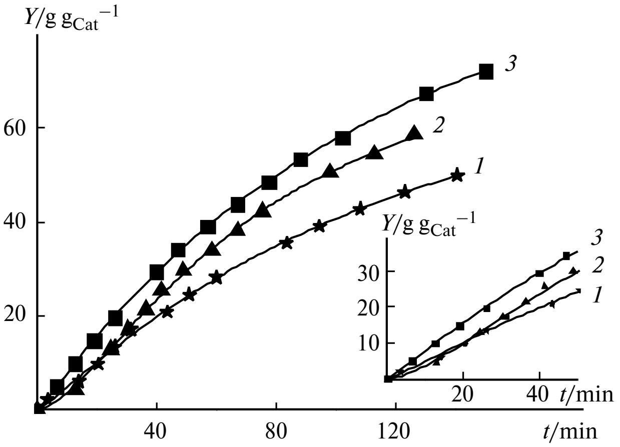

Fig. 1. Specific yield of polyketone as a function of the reaction time. Reaction mixture contains various amounts of MeOH (see Table 1, entries *1—3*): 3 (*1*), 4 (*2*), and 5 mL (*3*). Another protic agent is TsOH ($n(\text{TsOH})/n(\text{Pd}) = 4$).

tion of palladium and a fraction of Pd atoms formed metal and became inactive.[5,6]

The maximum activity of the supported catalysts is achieved at the high mole ratio $n(\text{MeOH})/n(\text{Pd})$ (5800). Evidently, MeOH takes part not only in the reactions leading to generation of active species but also in the formation of polymer molecules. The introduction of H_2O into the catalytic system changes the character of the kinetic curves. The kinetic curves of PK accumulation in the reactions using MeOH and a mixture of MeOH with H_2O are shown in Figs 1 and 2, respectively.

The reaction rate in the initial region of the kinetic curve increases with an increase in the amount of MeOH from 3 to 5 mL (see Fig. 1). A comparison of the kinetic curves recorded in the absence of water additives and upon the addition of 0.5 mL of H_2O (see Fig. 2, curves *1* and *2*) shows that the reaction rate in the initial region of the kinetic curve is lower in the presence of an H_2O additive, whereas at a longer reaction time the reaction rate is higher than that for the process without H_2O. This change in the character of the kinetic curves can be due to the formation of various types of active sites **1a** and **1b**. It is most likely that copolymerization involving hydride complexes **1b** is faster; however, the rate of their formation is low at small concentrations of water. The presence of maxima in the curves describing the dependence of the PK yield on the water content can be due to the change in the concentration of the active hydride complexes. The introduction of 2 mL of water resulted in a considerable decrease in the yield of the product and simultaneous formation of metallic palladium as evidenced by the appearance of gray color of the polymer product.

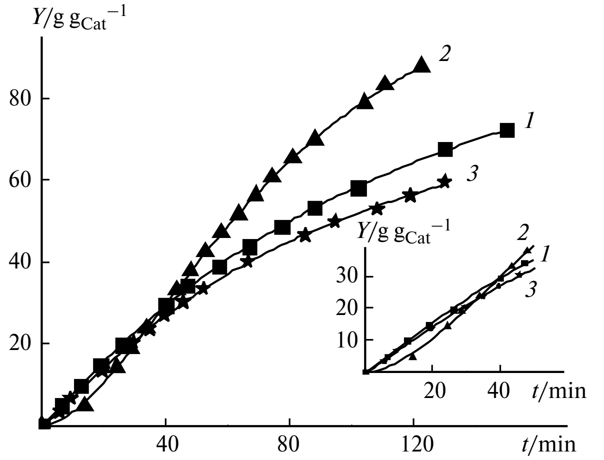

Fig. 2. Specific yield of polyketone as a function of the reaction time. Reaction mixture contains various amounts of H_2O (see Table 2, entries *1*, *3*, and *4*): 0 (*1*), 0.5 (*2*), and 1 mL (*3*). Other protic agents are MeOH (5 mL), TsOH ($n(\text{TsOH})/n(\text{Pd}) = 4$).

The presence of protic acids in the reaction medium is an important factor affecting the activity of the palladium catalysts in CO/olefin copolymerization. The study of the influence of the $n(\text{TsOH})/n(\text{Pd})$ ratio on the activity of $[\text{Pd(dppp)(TsO)(H}_2\text{O)](TsO)}$ in MeOH showed[10] that the activity of the catalyst reaches a maximum at the small mole ratio $n(\text{TsOH})/n(\text{Pd}) \approx 6$. Similar results were obtained[7] for the CO/ethylene copolymerization in the presence of Cat catalyst. The maximum activity of catalyst Cat was observed at the total ratio $n(\text{TsOH})/n(\text{Pd}) = 6$, and a further increase in the amount of the acid did not change the activity. These data confirm the commonly accepted point of view, according to which the acid stabilizes active intermediates **1b**.[5,10] Various acids, in particular, HCOOH, can be used to increase the rate of copolymerization. There are recent data indicating that this acid can also function as an agent of polymer chain termination and as an agent transforming the Pd^0 complexes into active hydride species **1b** (reactions (2) and (3)).[6]

$$L_2Pd^0 + H^+ \rightleftharpoons \mathbf{1b} \qquad (2)$$

$$L_2PdCH_2CH_2C(O)R^+ + HCOOH \longrightarrow$$

$$\longrightarrow CO_2 + \mathbf{1b} + MeCH_2C(O)R \qquad (3)$$

The data in Table 3 show that the specific yield of the CO/C_2H_4 copolymer changes in the presence of the supported catalysts in toluene upon the addition of various amounts of HCOOH.

The specific yield of the copolymer increases with an increase in the amount of HCOOH and attains a maximum value upon the introduction of 3 mL of HCOOH ($n(\text{HCOOH})/n(\text{Pd}) = 3900$ mol mol^{-1}). A comparison of two agents of polymer chain termination, MeOH and HCOOH, shows that the maximum specific yield of the product of the reaction for 2 h is close in these two cases, being 68.6—88.0 g g_{Cat}^{-1} (the experimental scatter of PK specific yield values is ±10%).

Table 3. Effect of the HCOOH content in the reaction mixture on the yield of polyketone

Entry	V_{HCOOH}/mL	n(HCOOH)/n(Pd)	Y*/g g_{Cat}^{-1}
1	1	1400	49.3
2	2	2600	61.0
3	3	3900	68.6
4	4	3800	56.3

* H_2O (0.5 mL) without MeOH was introduced into the reaction mixture. The reaction time was 2 h.

The dependences of the specific yield of PK on the reaction time in the presence of HCOOH/H_2O and upon the introduction of various amounts of HCOOH are shown in Fig. 3.

The reaction rate in the initial region increases with an increase in the amount of HCOOH, which can be due to an increase in the concentration of active species **1b**.

This work presents the results of studies of the alternating CO/ethylene copolymerization under the conditions non-typical for this process: toluene was used as a reaction medium, and the catalytic complex was introduced spread on a support. Nevertheless, the results obtained confirm the presently accepted scheme of the main reactions leading to the formation of active species and PK molecules. It has been shown for the first time that the maximum activity of the supported palladium catalyst is attained when MeOH (5 mL) and H_2O (0.5 mL) are simultaneously introduced. The protic agents participate in the in the reactions of polymer chain termination and in the formation of active species **1a** and **1b**. As a result of introduction of 0.5 mL of H_2O, the reaction rate at $t > 40$ min exceeds the rate of the process observed at smaller amounts of this agent in the system. This indicates higher rates of polymer growth on active hydride complexes **1b**. The addition of considerable amounts of water (2 mL and more) is accompanied by a sharp decrease in the catalyst activity, most likely, due to the formation of inactive forms of reduced palladium. The agent involved in the chain termination reaction can be HCOOH, *viz.*, acid, whose another function is to maintain a high concentration of the active hydride complexes. Fairly large amounts of HCOOH (3 mL) comparable with the quantity of the second agent of polymer chain termination (MeOH) should be introduced to design an active system. In these two cases, the specific yields of PK are comparable, being 68.6 and 88 g g_{Cat}^{-1} per 2 h, respectively.

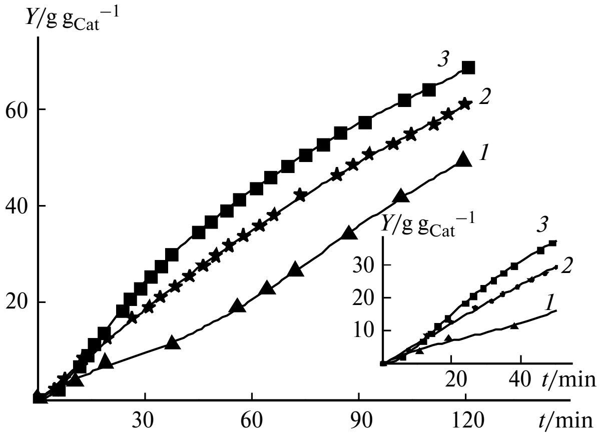

Fig. 3. Specific yield of polyketone as a function of the reaction time. Reaction mixture contains various amounts of HCOOH (see Table 3, entries *1—3*): 1 (*1*), 2 (*2*), and 3 mL (*3*). Another protic agent is H_2O (0.5 mL).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 11-03-00119).

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Received February 7, 2011;
in revised form March 18, 2011