Ethylene and carbon monoxide copolymerization catalyzed by supported palladium catalyst

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ABSTRACT

The kinetics of the copolymerization of ethylene with carbon monoxide catalyzed by (dppp)Pd(TsO)$_2$ (**I**) has been investigated under homogeneous conditions and in slurry with supported catalyst **I/P** (**P**: polymer support polyketone (PK)), at different catalyst concentrations. The specific rate reduced to gram of Pd of the initial stage of reaction is going up with increasing catalyst concentration, and the specific rate of the second macro-kinetic stage decreases with increasing catalyst loading.

The productivity of supported catalysts **I/P** and **I/SiO$_2$** has been analyzed in terms of the PK yield per gram of supported catalyst per hour. The specific copolymer yield increases with the increase in catalyst loading in **I/P** to 2×10^{-4} mol of Pd per 1 g of the supported catalyst and attains the maximum value of 27 $g_{PK}/(g_{sup.cat.} h)$ when copolymerization is carried out in the heptane–toluene mixture.

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1. Introduction

The reactions in which olefins copolymerize with carbon monoxide to form alternating polyketones have attracted great attention over past 20 years [1–3]. A greater number of researches were involved to study copolymerization in order to find new cheap and effective catalysts or to modify palladium (II) - biphosphine catalysts. Polyketones are generally synthesized in protic solvents in the presence of homogeneous catalysts based on palladium complexes with bi- and tridentate ligands, and Brønsted acids.

The use of supported catalysts in polymerization reactions is of interest in both fundamental and technological aspects. In particular, gas-phase and suspension processes in various media can be realized and various composite materials can be prepared. However only few patents report on approaches to the development of supported catalysts for the ethylene/CO copolymerization. For example, the first method of the preparation of a catalyst for gas-phase process was based on the use of polymer support–palladium complex solution mixture (patents by Shell Corp.) [4].

In our paper [5] we applied supported palladium catalysts formed as powder-like product in the copolymerization of ethylene with CO. It was shown that these catalysts are effective in the reaction of copolymerization of C$_2$H$_4$ with CO in heptane and toluene media, in the presence of a small amount of methanol, resulting in high polyketone yields. The effect of catalyst load-

ing on activity, product yield, and polymerization kinetics of the copolymerization of ethylene with CO using supported catalysts is an important question to be solved. The copolymerization of ethylene with CO can be carried out using various palladium complexes, bidentate ligands and acids. Both catalytic complex composition and reaction conditions can affect the kinetics of the process. Some contradictory data on the kinetics of copolymerization in homogeneous catalytic systems involving palladium complexes only can be found in publications. It is reported in Ref. [6] that the reaction rate of copolymerization with the [(dppp)Pd(H$_2$O)(TsO)](TsO) (dppp = Ph$_2$C(CH$_2$)$_3$CPh$_2$, TsO = CH$_3$C$_6$H$_4$SO$_3$) catalyst dissolved in methanol remains unchanged in time at [Pd] = $(0–1) \times 10^{-4}$ mol/L and grows linearly with the concentration of the catalyst. However kinetic curves are not given in Ref. [6], and there are no data on the time period at which the rate remains constant. Nevertheless, it is shown for the same catalyst that its productivity expressed in kg$_{PK}$/(g$_{Pd}$ h) at [Pd] = 3.2×10^{-5} mol/L decreases by 1.8 times with copolymerization time increasing from 1 to 6 h, which indicates a gradual rate decrease [7]. Kinetic curves for the copolymerization with the Pd(OAc)$_2$/dppp/HX catalytic system using different acids (HX = CF$_3$COOH, TsOH, HCOOH) in the methanol–toluene mixture at [Pd] = 4.8×10^{-4} mol/L are given in Ref. [8]. When the Pd(OAc)$_2$/dppp/TsOH catalytic system is used, the copolymerization rate decreases during 1 h. A 1.8-fold reaction rate decrease during 4 h when (dppp)Pd(CH$_3$CN)$_2$(BF$_4$)$_2$ dissolved in methanol is used, was also reported in Ref. [9] ([Pd] = 1.25×10^{-4} mol/L). Thus, it should be noted that when catalyst composition, reaction medium or copolymerization conditions are changed, kinetics of the reaction can noticeably change as well. Therefore, it is important to

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compare kinetic data for homogeneous systems and supported catalysts using the same palladium complex.

The main goal of the present work is to study the effect of catalyst loading on the activity of supported catalysts and the kinetics of copolymerization. Another goal is to study the kinetics of copolymerization using a homogeneous system at different catalyst concentrations to compare activity of a homogeneous catalyst and its supported analogue.

2. Experimental

2.1. Reagents and equipment

Palladium acetate (Pd(AcO)$_2$, 98% purity), 1,3-bis(diphenylphosphino)propane (dppp, 97%), and *p*-toluenesulfonic acid monohydrate (CH$_3$(C$_6$H$_4$)SO$_3$H·H$_2$O) (TsOH, 98% purity) were purchased from Aldrich.

Carbon monoxide and ethylene of 99.9% polymerization purity were used. Toluene and heptane were purified using a standard procedure and dried over molecular sieves 4 A. Methanol (0.5% of H$_2$O) was used without any purification.

IR spectra have been obtained with a PerkinElmer FT-IR spectrometer. Palladium content was measured by the spectrophotometry method using nitrozodiphenylamine. Specific surface area ($S_{sp.}$) of supports was measured by a static volumetric method on an Autosorb-1 instrument.

2.2. Preparation of catalysts

Pd(TsO)$_2$(dppp) (**I**) was synthesized as reported elsewhere [10] in a toluene–methanol mixture at a Pd(AcO)$_2$:dppp:TsOH = 1:1:2 ratio.

The procedure of supported catalysts preparation is described in Ref. [5]. Firstly, complex **I** was synthesized and the solvents were removed. Then elemental and spectral analyses of the product were performed. Calculated for C$_{41}$H$_{40}$O$_6$P$_2$S$_2$Pd (%): C, 57.18; H, 4.68; S, 7.45; Pd, 12.36. Found (%): C, 55.0; H, 4.3; S, 8.2; Pd, 12.0. The IR data are: ν_{P-C} (P–Ph, P–CH$_2$) 679–746 cm^{-1}; ν_{S-O} (SO$_3{}^-$) 1011–1220 cm^{-1}; δ_{CH_2} (–CH$_2$–) 1437 cm^{-1}; ν_{CH, CH_2} 2854.2, 2923.5 cm^{-1}. Subsequently **I** was adsorbed on supports. The solvent-free supported catalyst was prepared as dry powder placed into glass ampoules that have been thereafter evacuated and sealed.

Polymeric **P** (copolymer C$_2$H$_4$/CO) and inorganic **SiO$_2$** (silica gel) supports were used. The value of specific surface area was 10 m^2/g for **P** and 250 m^2/g for **SiO$_2$**.

2.3. Copolymerization

C$_2$H$_4$ was copolymerized with CO in a stainless steel reactor (V = 200 mL) equipped with a mechanical stirrer. Copolymerization on a homogeneous system and supported catalysts was performed using different techniques of catalyst introduction in the reactor. In the first case the reactor was pre-evacuated for 1 h and filled with a C$_2$H$_4$/CO mixture up to 1 atm pressure. Then catalyst solution (**I** dissolved in 55 mL of MeOH, 10 mL of toluene) and TsOH (TsOH/Pd = 4) dissolved in 5 mL of methanol were added to the reactor with a special syringe. The reactor was quickly heated to 90 °C upon stirring, and then the pressure was increased to 40 atm. This procedure was accomplished in 1–2 min. The kinetics was followed by measuring pressure dropping with time in a graduate vessel filled with the C$_2$H$_4$/CO mixture. Kinetic data were obtained by measuring the absorption of monomers with time and comparing the yield of polyketone (PK) at the end of the reaction with the amount of absorbed monomers. The discrepancy between these values was not higher than 10%. At the end of the experiment the reactor was

quickly cooled and pressure was reduced to 1 atm. The polymer was filtered off and dried.

The glass ampoule with the supported catalyst was fastened in the reactor which was then evacuated and filled with the C$_2$H$_4$/CO mixture at 1 atm pressure. Then the medium for suspension copolymerization (55 mL of heptane, 10 mL of toluene) was introduced with additives TsOH (TsOH/Pd = 4) and 5 mL of MeOH. The ampoule was broken upon simultaneous stirring, the reactor was quickly heated to 90 °C and pressure was increased to 40 atm during 1–2 min. Kinetic measurements were performed as described above.

3. Results and discussion

In order to compare the activity of a supported catalyst and related homogeneous system, the palladium complex (dppp)Pd(TsO)$_2$ (**I**) was used. The complex is characterized by a high activity in the copolymerization of C$_2$H$_4$ with CO [11]. It was shown [7] that TsOH acts as an activating agent in the copolymerization, and the catalytic system is most active at a TsOH/Pd molar ratio of 5–10. To provide similar conditions for the copolymerization using homogeneous system and supported catalysts, a TsOH/Pd molar ratio of 6 was applied. Since the palladium complex involves two TsO$^-$ counter-ions, in all cases TsOH was additionally introduced in a polymerization medium at a TsOH/Pd molar ratio of 4. The copolymerization was always realized under similar conditions, *i.e.* 90 °C, 40 atm pressure of C$_2$H$_4$/CO = 1/1 mixture.

3.1. Kinetics of CO/C$_2$H$_4$ copolymerization reaction

The kinetics of copolymerization was analyzed using a supported **I/P** catalyst at different contents of palladium in supported catalyst. The same palladium complex **I** was used as a catalyst in homogeneous conditions at different complex concentrations. The supported catalyst was prepared as dry powder and was introduced in a reactor in special glass ampoules sealed in vacuum. The content of **I** in the supported catalysts was determined using the content of Pd in the final product. Suspension copolymerization was performed in a heptane/toluene (55 mL/10 mL) mixture. The complex **I** was insoluble in this medium, and palladium was not found in the liquid phase. A small amount of methanol (5 mL) and TsOH (TsOH/Pd = 4 mol/mol) was introduced as activating agents in the reaction medium. The supported catalyst productivity was analyzed from the measurements of copolymer yield calculated per 1 g of the supported catalyst. The supported catalyst weight involves those of a support and a palladium compound:

$$P_{\text{sup.cat.}} = P_{\text{support}} + P_{\textbf{I}}$$

The activity of supported catalysts can be expressed in different units, *e.g.* per gram of supported catalysts or gram of Pd. The following symbols will be used below for the calculations of PK yield, copolymerization rate and catalytic activity:

W – rate of copolymerization, g$_{PK}$/min;

W_A – rate of copolymerization expressed in kg$_{PK}$/(g$_{Pd}$ h);

$W_{\text{sup.}}$ – copolymerization rate per gram of supported catalyst, g$_{PK}$/(g$_{\text{sup.cat.}}$ min);

Y – yield of PK per gram of Pd, kg$_{PK}$/g$_{Pd}$;

$Y_{\text{sup.}}$ – PK yield per gram of supported catalyst, g$_{PK}$/g$_{\text{sup.cat.}}$ and

A – productivity of supported catalysts determined from an averaged polymer yield per gram of supported catalyst, per time unit, g$_{PK}$/(g$_{\text{sup.cat.}}$ h).

The CO/C$_2$H$_4$ copolymerization reaction proceeds in the presence of supported **I/P** with the increase in PK yield with increasing
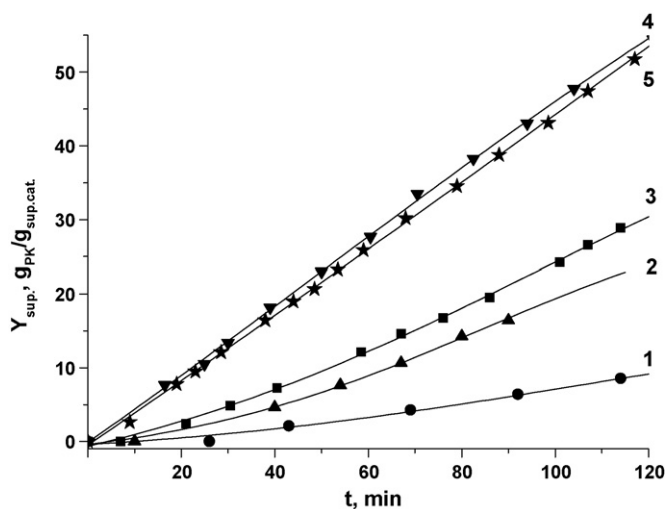
Fig. 1. The time dependence of specific polyketone yield at different catalyst loadings in supported catalyst **I/P**. The values of catalyst loading $[\mathbf{I}]_{sup.cat.}$ (in 10^{-4} mol/$g_{sup.cat.}$) are: 1 – 0.5; 2 – 0.7; 3 – 1; 4 – 2; 5 – 3. Reaction conditions: 90 °C, $CO/C_2H_4 = 1/1$, 40 atm, copolymerization medium: heptane 55 mL, toluene 10 mL. Additives: MeOH 5 mL, TsOH/Pd = 4 mol/mol.

catalyst loading in supported catalyst. The time dependence of PK yield reduced per gram of supported catalyst at different palladium contents in these catalysts is shown in Fig. 1.

The copolymerization reaction catalyzed by **I/P** containing $(0.5–0.7) \times 10^{-4}$ mol of Pd per gram of the supported catalyst (curves 1 and 2) proceeds with a long induction period (25–15 min). PK yield per gram of supported catalyst is growing with increasing palladium content up to 2×10^{-4} mol of Pd per gram of the catalyst, and remained unchanged with a further increase in the palladium content; a similar yield of PK calculated per gram of the supported catalyst was observed for the catalyst loading of 2×10^{-4} and 3×10^{-4} mol/g in supported catalyst (curves 4 and 5 in Fig. 1). The analysis of the obtained kinetic data in terms of PK yield per gram of Pd reveals a complex character of kinetic regularities, as is shown in Fig. 2.

The kinetic curves change in a complex manner with the catalyst concentration. The rate reduced to gram of Pd on the initial stage of
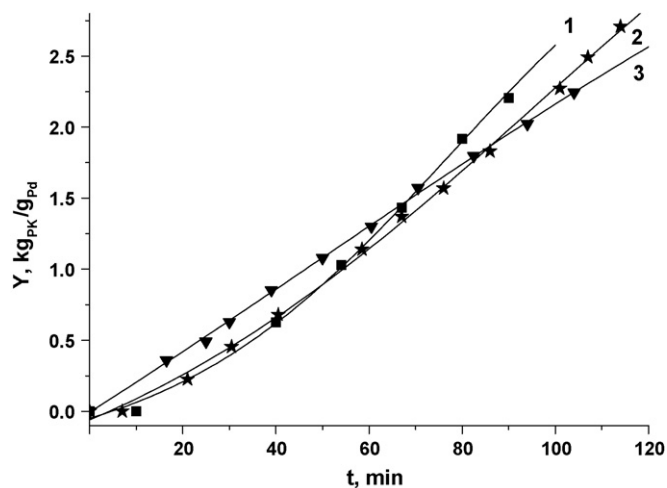

Fig. 2. The time dependence of polyketone yield reduced to gram of Pd at different catalyst loadings in supported catalyst **I/P**. The values of catalyst loading $[\mathbf{I}]_{sup.cat.}$ (in 10^{-4} mol/$g_{sup.cat.}$) are: 1 – 0.7; 2 – 1; 3 – 2. Reaction conditions: 90 °C, $CO/C_2H_4 = 1/1$, 40 atm, copolymerization medium: heptane 55 mL, toluene 10 mL. Additives: MeOH 5 mL, TsOH/Pd = 4 mol/mol.
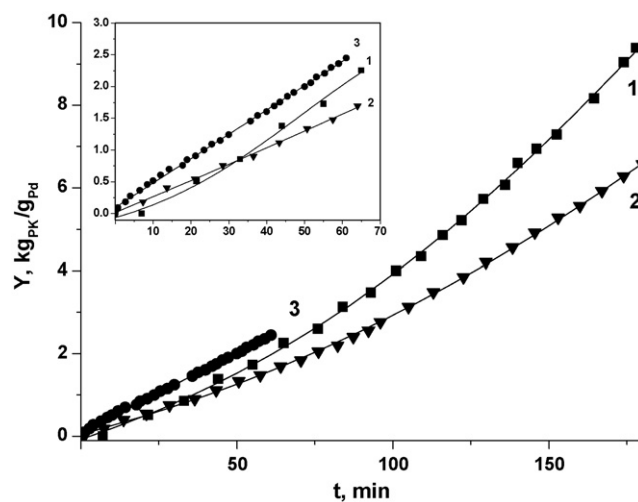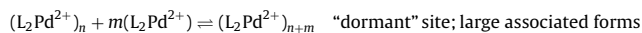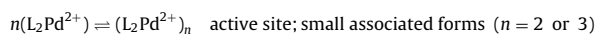

Fig. 3. The time dependence of polyketone yield reduced to gram of Pd. CO/C_2H_4 copolymerization under homogeneous conditions, at different $(dppp)Pd(TsO)_2$ (**I**) concentrations. $[\mathbf{I}] \times 10^4$ mol/L: 1 – 1.0; 2 – 2.4; 3 – 5.6. Reaction conditions: 90 °C, $CO/C_2H_4 = 1/1$, 40 atm, MeOH 60 mL, toluene 10 mL. Additive: TsOH/Pd = 4 mol/mol.

the reaction increases with increasing palladium content, but after 60 min the specific rate decreases with increasing catalyst loading. Analogous kinetic data were obtained for the homogeneous system at different **I** concentrations. The PK yield from time reduced to gram of Pd is presented in Fig. 3.

The initial copolymerization rate reduced to gram of Pd grows with increasing [**I**] from 1 to 5.6×10^{-4} mol/L. After the initial period, the second stage with an almost constant copolymerization rate is observed in all cases. The specific rate of this period in $kg_{PK}/(g_{Pd}$ min) was higher at low concentration of 1×10^{-4} mol/L and weakly changed in the $(2–5.6) \times 10^{-4}$ mol/L concentration range. Thus two sections of the kinetic curves can be considered. The experimental technique prevents from analyzing initial rates during the first minute of the reaction, and hence the rate W1 was measured at $t = 10$ min in g_{PK}/min. The rate of the second stage W2 was determined at $t = 120$ min, and in the case of the highest concentration of 5.6×10^{-4} mol/L W2 was measured at $t = 60$ min. The dependence of W1 and W2 on the catalyst concentration in the homogeneous system (a) and on the catalyst loading in supported catalyst (b) is given in Fig. 4.

The analysis shows that W2 varies as a square root of concentration in both cases and in the initial stage of reaction the reaction order on catalyst concentration is higher than 1, approaching to 2. Hypothetically this can result from the participation of associated forms of palladium compounds in the reaction. It is possible that small associates like dimeric or trimeric forms are active sites. On the other hand, the second stage of the reaction is characterized by some decrease in the rate reduced to gram of Pd with the increasing catalyst concentration. Some reduction of specific rate on the second stage of reaction at high palladium concentrations can be caused by aggregation of small associates in larger associated forms. However at high concentration the catalyst shows stable catalytic behaviour; i.e. the process of formation of large associates does not lead to a deactivation of the catalyst. The latter is supposed to form "dormant" sites:

$$n(L_2Pd^{2+}) \rightleftharpoons (L_2Pd^{2+})_n \quad \text{active site; small associated forms } (n = 2 \text{ or } 3)$$

$$(L_2Pd^{2+})_n + m(L_2Pd^{2+}) \rightleftharpoons (L_2Pd^{2+})_{n+m} \quad \text{"dormant" site; large associated forms}$$

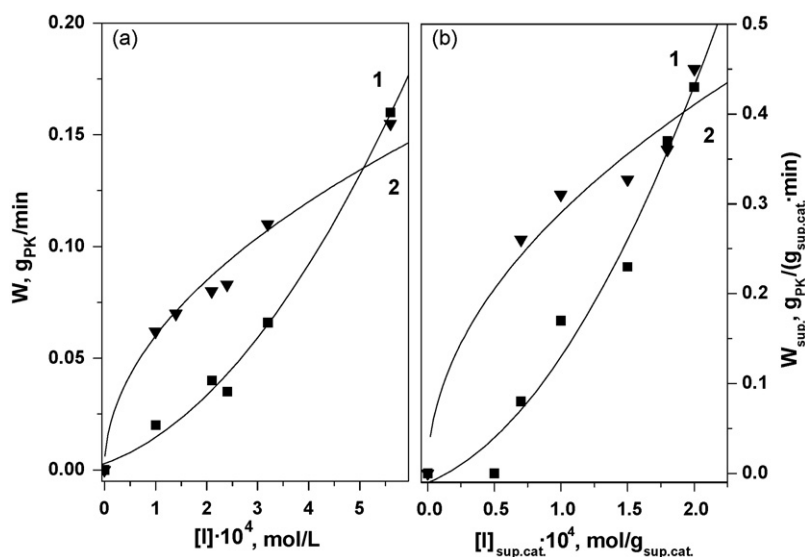These assumptions are confirmed by the following experimental data:

Fig. 4. The dependence of copolymerization rates W1 (1) and W2 (2) on catalyst concentration under homogeneous conditions (a, reaction conditions: 90 °C, $C_2H_4/CO = 1/1$, 40 atm, MeOH 60 mL, toluene 10 mL. Additive: TsOH/Pd = 4 mol/mol) and on catalyst loading in supported **I/P** (b, reaction conditions: 90 °C, $C_2H_4/CO = 1/1$, 40 atm, copolymerization medium: heptane 55 mL, toluene 10 mL. Additives: MeOH 5 mL, TsOH/Pd = 4 mol/mol).

- induction periods were observed at low catalyst concentrations; in the case of supported catalyst, induction period reaches to 25 min at the catalyst loading of 5×10^{-5} mol/$g_{sup.cat.}$;
- maximum of PK yield on supported catalyst was observed at a rather high catalyst loading of $(2-3) \times 10^{-4}$ mol/$g_{sup.cat.}$ in the polymer-supported catalyst and
- the reaction in the second stage is characterized by a constant rate even at high catalyst loadings in supported catalyst; there was no catalyst deactivation during 3 h at a palladium content of 3×10^{-4} mol/g in **I/P**. The overall PK yield in this case was equal to 80 g/g of support.

Some literature data confirm these assumptions. It is known that palladium complexes can form associated structures: for example, palladium acetate exists as a trimeric form in benzene solution and

in the solid state [12]. Dinuclear palladium complexes show high activity in CO–ethylene copolymerization reaction [13]. At present, only kinetic data point to the possible participation of palladium associated forms in the copolymerization reaction, although the structure of these forms could not be suggested in this stage of investigation.

In general, the activity of palladium catalysts in copolymerization is estimated from PK yield calculated per gram of Pd per hour. However the observed complex character of the kinetics results in a high experimental point scattering for this value. Nevertheless, the values of $W2_A$ expressed in the same units, $kg_{PK}/(g_{Pd}\,h)$, vary depending on catalyst concentration with small experimental point scattering, and this parameter can be used to estimate the catalytic activity. The comparison of activity of a homogeneous system (a) and that based on supported catalyst (b) is presented in Fig. 5.
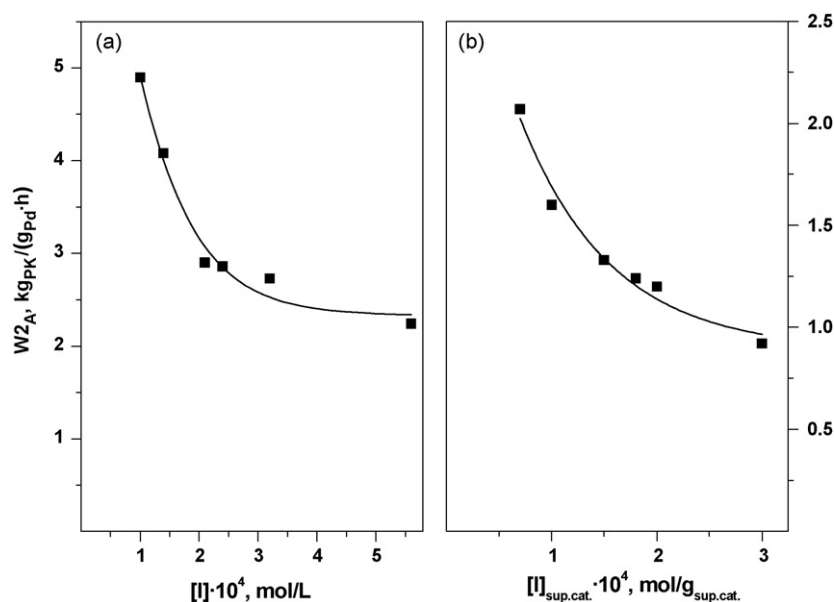

Fig. 5. The dependence of specific rate W2 on catalyst concentration in copolymerization reaction under homogeneous conditions (a, reaction conditions: 90 °C, $C_2H_4/CO = 1/1$, 40 atm, MeOH 60 mL, toluene 10 mL. Additive: TsOH/Pd = 4 mol/mol) and on catalyst loading in supported **I/P** (b, reaction conditions: 90 °C, $C_2H_4/CO = 1/1$, 40 atm, copolymerization medium: heptane 55 mL, toluene 10 mL. Additives: MeOH 5 mL, TsOH/Pd = 4 mol/mol).
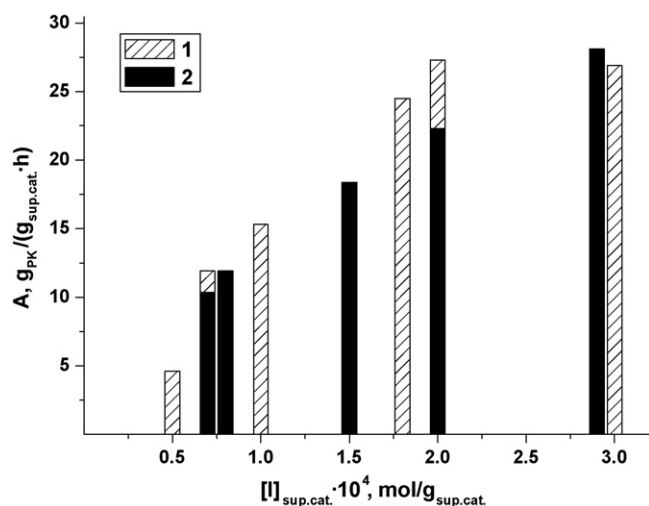
Fig. 6. The dependence of average productivity for $t = 2$ h of the supported catalysts **I/P** (1) and **I/SiO$_2$** (2) on palladium content in catalysts. Reaction conditions: 90 °C, CO/C$_2$H$_4$ = 1/1, 40 atm, copolymerization medium: heptane 55 mL, toluene 10 mL. Additives: MeOH 5 mL, TsOH/Pd = 4 mol/mol.

The values of W2$_A$ in the case of copolymerization under homogeneous conditions change in the range (2.3–4.9) kg$_{PK}$/(g$_{Pd}$ h) at the catalyst concentrations of $(5.6–1) \times 10^{-4}$ mol/L. W2$_A$ weakly changes in a wide concentration range $(2–5) \times 10^{-4}$ mol/L, and on average is equal to 2.5 kg$_{PK}$/(g$_{Pd}$ h). When copolymerization reaction is catalyzed by supported **I/P**, the value of W2$_A$ changes in the range (0.9–2) kg$_{PK}$/(g$_{Pd}$ h). Thus in the case of supported catalyst, W2$_A$ is by 2.8–1.3 times lower than average copolymerization rate in a homogeneous system. This reduction of activity per gram of Pd is probably due to high catalyst concentration on support surface at palladium contents higher than 2×10^{-4} mol/g$_{sup.cat.}$.

3.2. Productivity of supported catalysts

The productivity of supported catalysts can be estimated from the yield of copolymer calculated per gram of the supported catalyst per hour (g$_{PK}$/(g$_{sup.cat.}$ h)). However the complex pattern of kinetic regularities results in high values of experimental data scattering for polymer yield within a small period of time (e.g. 1 h). Then the values of productivity were calculated from the average yield of copolymer for 2 h of the reaction.

The analysis of the productivity dependence on the palladium content is very important for the understanding of the mechanism of copolymer formation with supported catalyst. If the copolymer is formed on the particles of supported catalyst only, a limiting value of productivity should exist, which corresponds to a certain total content of Pd in supported catalyst . Depending on the specific surface area of the support, the limiting value of productivity can be attained at a different Pd content. To analyze the dependence of the catalyst productivity on the content of palladium, we used two types of support, namely, polymeric **P** and inorganic **SiO$_2$**. These supports are characterized by different specific surface areas, 10 and 250 m^2/g, respectively. Copolymer yield in the copolymerization reaction using supported catalysts **I/P** and **I/SiO$_2$** is presented in Fig. 6.

The productivity of supported catalyst **I/P** increases with increasing palladium content up to 2×10^{-4} mol/g$_{sup.cat.}$. The product yield calculated per gram of supported catalyst equals ~27 g$_{PK}$/(g$_{sup.cat.}$ h) at the palladium content of about $(2–3) \times 10^{-4}$ mol/g$_{sup.cat.}$. This fact evidences that polyketone is formed on supported catalyst particles and at a high palladium

content in a catalyst, only a part of catalyst molecules being involved in the reaction. The support **P** is characterized by a specific surface value of 10 m^2/g. A simple estimation based on the value of amount of Pd atoms per a unit of surface area of the support shows that the distance between palladium atoms should be close to 2.9 Å at a catalyst loading of 2×10^{-4} mol/g$_{sup.cat.}$. This implies that the support surface is "saturated" by a catalyst at the high palladium content. The calculated value of the distance between palladium atoms can be compared with the following data: the Pd–Pd distance in different crystalline modifications of Pd(OAc)$_2$ changes from 2.92 to 3.2 Å [14]. A similar dependence of PK yield per gram of supported catalyst from palladium content was obtained for **I/SiO$_2$** catalyst. However, the productivity grew with the increasing palladium content up to 3×10^{-4} mol/g$_{sup.cat.}$. Obviously, the effect of surface "saturation" was not achieved at a high palladium content of 3×10^{-4} mol/g$_{sup.cat.}$ so far as the specific surface of **SiO$_2$** is equal to 250 m^2/g.

4. Conclusions

The kinetics of C$_2$H$_4$/CO copolymerization catalyzed by the homogeneous (dppp)Pd(TsO)$_2$ (**I**) and supported **I/P** catalysts changes in a complex mode with catalyst concentration. In the initial stage, copolymerization rate follows a kinetics low with the order >1 on the catalyst concentration. The rate of the second kinetic stage of copolymerization reduced to gram of Pd decreases with catalyst concentration increasing. In the case of homogeneous system at [**I**] = $(2–5) \times 10^{-4}$ mol/L the copolymerization rate equals on average 2.5 kg$_{PK}$/(g$_{Pd}$ h), and for the supported catalyst **I/P** the rate changes in the range (2–0.9) kg$_{PK}$/(g$_{Pd}$ h) with increasing [**I**]$_{sup.cat.}$ from 7×10^{-5} to 3×10^{-4} mol/g$_{sup.cat.}$. Thus the activity of supported catalysts calculated per gram of palladium is lower than the activity of a homogeneous system because at a high concentration of palladium on the support surface only a part of Pd atoms participate in the reaction.

The polyketone (PK) yield per gram of supported catalyst **I/P** increases up to 27 g$_{PK}$/(g$_{sup.cat.}$ h) with the content of palladium increasing to 2×10^{-4} mol/g$_{sup.cat.}$. The further increase in catalyst loading does not result in the increase of the copolymerization rate and specific yield of PK. Thus in the case of polymeric support **P** with specific surface area of 10 m^2/g the optimum content of palladium is ~2×10^{-4} mol/g$_{sup.cat.}$. For **SiO$_2$** support with specific surface area of 250 m^2/g, this value is higher than 3×10^{-4} mol/g$_{sup.cat.}$.

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