# Electrospray mass spectrometric study of homogeneous catalytic system $Pd(CF_3COO)_2—Ph_2P(CH_2)_3PPh_2—MeOH/Me_2CO—H_2O$ for copolymerization of ethylene and carbon monoxide

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The catalytic system $Pd(CF_3COO)_2—Ph_2P(CH_2)_3PPh_2—MeOH/Me_2CO$ was studied by electrospray mass spectrometry. The $\{[Pd(dppp)_2]^{2+}$, $[(dppp)_2Pd(CF_3COO)]^+$, $[(dppp)Pd(CF_3COO)]^+$, and $[(dppp)Pd(CF_3COO)_2Pd(dppp)]^{2+}\}$ cations were found in the system. The addition of $H_2O$ to the system resulted in the formation of binuclear bicharged ions $[(dppp)Pd(OH)]_2{}^{2+}$ and their associates with water.

**Key words:** copolymerization of $C_2H_4$ and CO, electrospray mass spectrometry, palladium complexes.

It is known that a Pd-containing homogeneous system modified with an organophosphorus ligand and a weakly coordinating anion of a Brönsted acid in a polar medium is a catalyst of copolymerization of ethylene and carbon monoxide,[1—6] which evokes interest in the study of these systems.[7—10]

In this work, we present data on a study of the ionic composition of the catalytic system $Pd(CF_3COO)_2—Ph_2P(CH_2)_3PPh_2—MeOH/Me_2CO—H_2O$ by time-of-flight mass spectrometry with extraction of dissolved ions by electrospraying of the liquid at atmospheric pressure (electrospray mass spectrometry). This method makes it possible to transfer existing ions from solution to the gas phase under mild conditions[11] and to record their mass spectra. The construction of an ion source provides the possibility of controlling the intrinsic temperature of ions moving through a rarefied gas in the first step of differential evacuation and, hence, of controlling their fragmentation. This is achieved by a change in the electric field strength $\Delta U$.

## Experimental

The salt $Pd(CF_3COO)_2$ for the preparation of the catalyst was obtained by the known procedure.[12] The reference complex $Pd(dppp)Cl_2$ was synthesized by the procedure described previously.[13]

To prepare the catalyst, 0.216 g (1 mmol) of $Pd(CF_3COO)_2$ and 0.55 g (1.33 mmol) of dppp were dissolved separately in 20 mL of methanol containing 1.5 wt. % of $H_2O$. A suspension obtained by mixing of two solutions was stirred for 1 h at room temperature and then filtered off. A portion of the solvent was removed from a filtrate on heating to 50 °C. Anhydrous ethyl ether (~200 mL) was added dropwise to the remaining solution to precipitate a white powder, which was filtered off, washed with anhydrous hexane, and dried *in vacuo* at 70 °C. The active homogeneous catalyst for copolymerization of $C_2H_4$ and CO was obtained by dissolution of the dry substance in methanol.

Solutions of the active catalyst were studied on a time-of-flight mass spectrometer of the mass-reflectron type with extraction of dissolved ions at atmospheric pressure as described previously.[14,15] An aqueous-ethanol or ethanol solution of the catalyst was injected into an ion source with a velocity of 2 $\mu L\ min^{-1}$ through a metallic capillary with an internal diameter of 0.1 mm. The application of voltage of ~2 kV to the capillary results in finely disperse spraying of the solution analyzed, and the final stage of the spraying is the field evaporation of the ions contained in the liquid. A portion of these ions is transported to a mass analyzer through a vacuum interface with differential evacuation. An increase in the electric field strength ($\Delta U$) at the first step of differential evacuation, where the gas pressure is 5 Torr, increases the kinetic energy of ions and, hence, the probability of their fragmentation upon collisions. The comparison of the spectra obtained at various $\Delta U$ values is often useful for obtaining information about the structure of ions studied.

## Results and Discussion

The mass spectrum of the catalytic homogeneous system studied is presented in Fig. 1. The integers near the peaks (lines) denote the positions of the maxima in

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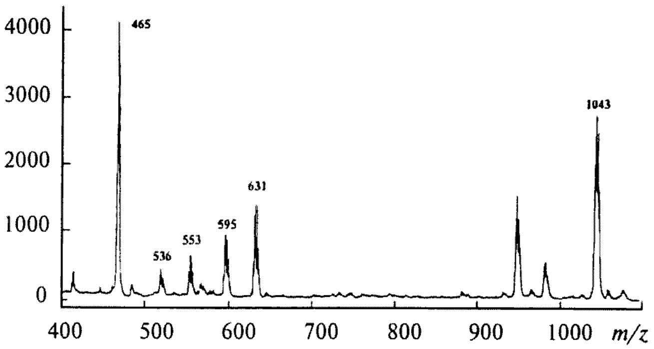

**Fig. 1.** Mass spectrum of positive ions isolated from an aqueous—alcohol solution of the catalyst.

the isotope mass distribution on the $m/z$ scale. The position and structure of the line with $m/z = 465$, which has a maximum intensity at low (lower than 200 V) $\Delta U$ values in the spectra obtained, coincide with those of the line of the $[Pd(dppp)_2]^{2+}$ ion formed when the $[Pd(dppp)_2](CF_3COO)_2$ complex is dissolved in methanol.[16] It has been established previously[16] that an increase in the intrinsic energy of the $[Pd(dppp)_2]^{2+}$ ion as $\Delta U$ increases results in the formation of $[Pd(dppp)Ph]^+$ ($m/z = 595$) and $[dppp\text{-}Ph]^+$ ($m/z = 335$) ions.

The peak with $m/z = 1043$ (second in intensity) is caused by the $[(dppp)_2Pd(CF_3COO)]^+$ ion, which is likely the associate of the bicharged cation $[(dppp)_2Pd]^{2+}$ with anion $CF_3COO^-$, and the anion is present in the outer coordination sphere of the palladium complex. However, a possible short contact of the anion with the metal cannot be ruled out. In this case, one or both dppp ligands should be monodentate. The latter seems quite probable, and a change in the dentate character of the phosphine ligands can explain the necessary coordination unsaturation upon catalysis.

Two probable structures can also be suggested for the peak with $m/z = 631$: $[(dppp)Pd(CF_3COO)]^+$ and $[(dppp)Pd(CF_3COO)_2Pd(dppp)]^{2+}$, where $CF_3COO^-$ is a bridge between the metal atoms. The analysis of the shape of the line showed that the contribution from the bicharged species decreases as $\Delta U$ increases.

The origin of the line with $m/z = 553$ appearing in the spectra of some samples is associated with a chlorine admixture. This follows from the examination of the shape of the line (Fig. 2) as well as from the analysis of the dry catalyst performed by chemical methods and X-ray photoelectron spectroscopy. As seen from Fig. 2, the shape of the peak with $m/z = 553$ changes considerably as $\Delta U$ changes. The analysis of the shape shows that the fraction of the bicharged $[(dppp)PdCl_2Pd(dppp)]^{2+}$ ions can decrease efficiently as $\Delta U$ increases, and the fraction of the monocharged $[(dppp)PdCl]^+$ ions, on the contrary, increases. No correlation between the catalyst activity and the chlorine content in it has been established so far.[7] The chlorine admixture is explained by insufficient purification of the initial salt $Pd(CF_3COO)_2$ obtained from $PdCl_2$.

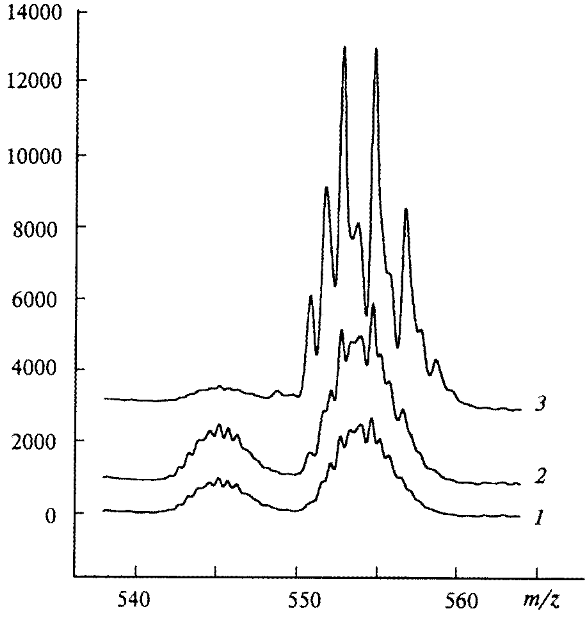

**Fig. 2.** Change in the form of the peak with a maximum at $m/z = 553$ for $\Delta U$/V: 100 (*1*), 150 (*2*), 200 (*3*).

The activity of analogous homogeneous systems is often explained by the presence of water in one or another form.[17–18] As mentioned previously,[7] O—H fragments are present in the dry catalyst (the IR spectrum of the dry catalyst contains a broad absorption band at 3340 cm$^{-1}$). In the mass spectrum of the catalyst obtained by dissolution of the dry substance in anhydrous methanol, no peaks, which could be assigned to the ions containing $H_2O$ and/or OH, were observed (Fig. 3, spectrum *1*). However, it cannot be excluded that the peak with $m/z = 553$ assigned to the $[(dppp)PdCl]^+$ ion is partially caused by associate $[(dppp)Pd(OH)(H_2O)]_2^{2+}$, which in principle can be observed in the spectra at low $\Delta U$ values. The absence of the peaks related to aqua-containing ions is caused by the fact that anhydrous alcohol binds water. The addition of water to the catalyst results in the formation of $[(dppp)Pd(OH)]_2^{2+}$ ions ($m/z = 536$) and $[(dppp)Pd(OH)]_2^{2+} \cdot H_2O$ associates ($m/z = 545$) (see Fig. 3, spectrum *2*). The latter appear only at low values of $\Delta U$. This coincides with the published data,[19] which state that coordination water breaks away from positive ions even at low values of $\Delta U$ (lower than 100 V).

Thus, the studies performed have shown that the $Pd(CF_3COO)_2—Ph_2P(CH_2)_3PPh_2—MeOH/Me_2CO—H_2O$ system, which is catalytically active in copolymer-

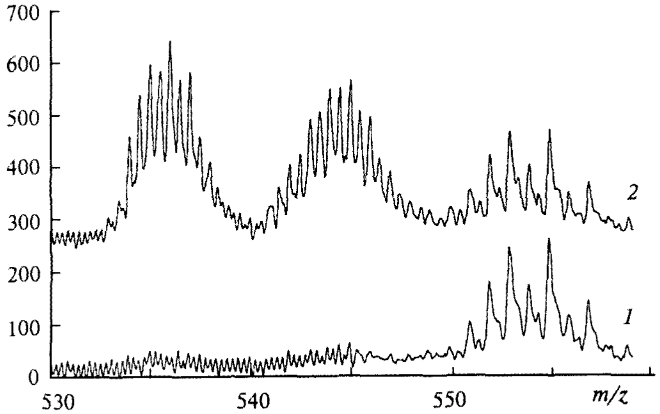

**Fig. 3.** Mass spectra of the catalyst prepared using anhydrous alcohol before (*1*) and immediately after addition of water (*2*).

ization of ethylene and carbon monoxide, contains several positive ions $\{[Pd(dppp)_2]^{2+}$, $[(dppp)_2Pd(CF_3COO)]^+$, $[(dppp)Pd(CF_3COO)]^+$, and $[(dppp)Pd(CF_3COO)_2Pd(dppp)]^{2+}\}$, and the concentration of the $[Pd(dppp)_2]^{2+}$ ion is greater than those of the other ions. The admixture of the chlorine-containing ions $[(dppp)PdCl_2Pd(dppp)]^{2+}$ and $[(dppp)PdCl]^+$ found in some samples is explained by insufficient purification of the initial salt $Pd(CF_3COO)_2$, which was obtained from $PdCl_2$. The addition of water to the system results in the formation of the binuclear bicharged $[(dppp)Pd(OH)]_2^{2+}$ ions, many of which can be surrounded by the "coat" of polar molecules in the reaction system. MeOH and $H_2O$ can act as such molecules, which is testified by the appearance of the $[(dppp)Pd(OH)]_2^{2+} \cdot H_2O$ associates in the mass-spectrum.

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