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Kinetics and Mechanism of Palladium(II) Acetate Reduction by Hydrogen on the Surface of a Carbon Support

A. S. Berenblyum*, Hussein Ali Al-Wadhaf, E. A. Katsman, and V. R. Flid

Moscow State Academy of Fine Chemical Technology, Moscow, 119571 Russia

** e-mail: ayb@go.ru*

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Abstract—The kinetics of the reduction of Pd(II) compounds by dihydrogen on the surface of a carbon support has been investigated for palladium acetate as an example. A kinetic model has been constructed for this reaction. An autocatalytic mechanism is suggested, in which the key role is played by Pd(0) compounds and their hydrides. The reaction occurring on the support surface is compared with the same reaction in solutions of palladium phosphine acetate complexes, where a similar mechanism is observed. One of the most important features of the surface reaction is the relatively slow reduction of the Pd(I) compounds to Pd(0). This makes it possible to obtain materials with a high Pd(I) content of 5% and above.

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Supported palladium catalysts are widely used in large-scale-processes of the petrochemical and petroleum refining industries, including the hydrogenation of unsaturated compounds, dehydrogenation, isomerization, and hydrogenolysis [1, 2]. In recent years, much attention has been given to developing the scientific foundations of the preparation of these catalysts, particularly their synthesis, structure, and physicochemical properties [3–5]. The sustained striving towards better catalysts, primarily more active and more selective ones, prompts researchers to study catalyst preparation chemistry in greater detail.

A conventional way of preparing metal catalysts, including palladium ones, is by loading a support with the initial palladium compound followed by the reduction of this compound [6]. Therefore, for obtaining advanced, highly efficient catalysts, it is necessary to investigate the processes occurring on the support surface, including the reduction of the palladium precursor, in which palladium is usually in the oxidation state +2, into its active state.

Although there have been lots of publications dealing with heterogeneous catalysts, the reduction mechanisms of the catalysts precursors on support surfaces are still poorly understood. Obviously, knowledge of these mechanisms is quite essential for correctly selecting a precursor, obtaining finely dispersed metal catalysts, etc. In addition, investigation of the chemistry of these complicated solid-phase surface reactions is of fundamental interest as a way to elucidate the effect of the surface on these reactions.

When investigating reactions on support surfaces, researchers encounter difficulties typical for surface studies, including the problem of choosing an appropriate method for monitoring the conversion of surface compounds and, thereby, the reaction kinetics.

Here, we report the kinetics and mechanism of the reduction of supported palladium(II) acetate with hydrogen, a widespread reductant in the synthesis of supported metal catalysts [7, 8].

EXPERIMENTAL

Chemicals, Materials, and Their Purity

The following chemicals were used: palladium acetate (reagent grade) as received, acetone (special-purity grade), hydrogen gas (brand A, 99.99%), and nitrogen gas (special-purity grade, 99.999%).

The support was Vulcan XC-72 carbon with a specific surface area of about 250 m^2/g [9]. Prior to catalyst synthesis, the support was annealed in an oxygen atmosphere at 450°C for 4 h [10].

Synthesis of Carbon-Supported Palladium(II) Acetate

Acetone (50 ml) was added to carbon (500 mg), and the mixture was ultrasonicated at room temperature for 20 min to obtain a homogeneous suspension. An appropriate amount of a palladium acetate dissolved in 15 ml of acetone was added to the suspension, and the mixture was stirred for 15 min. Next, the entire solvent was evaporated in a rotary evaporator under careful heating. Samples containing 2.0, 4.0, and 9.1 wt % Pd (relative to the palladium + support weight) were thus obtained.

Kinetic Experiments

Palladium acetate reduction by hydrogen takes place according to the following overall chemical equation:

$$Pd(OAc)_2 + H_2 \longrightarrow Pd + 2HOAc.$$

A sample (0.1 g) was placed in a tubular reactor, and hydrogen at a preset partial pressure was passed through the reactor. The total absolute gas pressure was 1 atm, and the desired hydrogen partial pressure was obtained by diluting hydrogen with nitrogen. The acetic acid resulting from the reaction was carried away by the hydrogen stream and then by a nitrogen stream and was absorbed by a solution of an excess amount of an alkali. After the run, the alkali was titrated with hydrochloric acid. The experimental setup, the reduction procedure, and the quantification of acetic acid by titration were described in detail in an earlier publication [10]. The error of acetic acid determination did not exceed 7 rel. %. Special-purpose experiments demonstrated that, at the hydrogen feed rate used in our experiments (0.72 l/h), there are no significant external diffusion limitations [10]. In order to see whether there are internal diffusion limitations, we examined a support sample in which ~80% of the particles were 0.40–3.20 mm in diameter, much larger than those used in standard kinetic runs (<0.01 mm). It was found that the acetic acid evolution rates for the standard catalyst sample and for the sample synthesized using large carbon particles are equal within the experimental error. Therefore, for the carbon particles sizes below 0.01 mm, the internal diffusion limitations in the reaction between hydrogen and palladium acetate can be neglected.

Spectroscopic Methods

X-ray photoelectron spectra were recorded on an XSAM-800 spectrometer (Kratos, United Kingdom). The X-ray source was a magnesium anode with a characteristic MgK_α radiation energy of 1253.6 eV. The maximum power dissipation in the anode during spectrum recording was 90 W. The background due to the secondary electrons and the photoelectrons that had lost energy was approximated by a straight line. Measurements were taken at a pressure of $\sim 5 \times 10^{-8}$ Pa. The samples were secured on a sample holder with a conductive double-sided adhesive tape. Spectra were obtained at room temperature. The spectrometer was calibrated against the Au $4f_{7/2}$ and Ni $2p_{3/2}$ peaks, whose binding energies are 84.0 and 852.7 eV, respectively.

IR spectra were recorded for KBr pellets on a Digilab Scimitar 1000 IR Fourier transform spectrometer (Varian).

Kinetic Data Processing

The following three programs were used in the construction of the kinetic model.

Direct kinetic problem solver [11, 12]. This program employs the subprogram STIFF [13] in the numerical integration of sets of ordinary differential equations. It enables one to calculate not only the reactant concentrations, including the acetic acid concentration, at preset points in time, but also other components of the observation model (so-called responses) for a given kinetic model [11, 12, 14]. Here, the concentrations of palladium in the oxidation states +2, +1, and 0 are meant. Analyzing the responses, we evaluated the goodness of fit between the calculated and observed data. The measure of the goodness of fit was the objective function (functional) defined as the square root of the average sum of the weighted squares of the differences between the calculated and observed values. The weighting factors were the inverse squares of the standard measurement error [11] for the corresponding responses. In other words, the goodness of fit was nothing else but the standard deviation between the calculation and the experiment in terms of standard response measurement errors. If a kinetic model is in good agreement with the experimental data, the goodness of fit is close to unity; if the goodness of fit is well above unity, the model is considered to be invalid [11, 14].

Inverse kinetic problem solver (numerical estimation of kinetic model parameters) [11, 12]. This program is based on the least-squares method [11]. It minimizes the functional by the configuration method [15]. The search step size in the minimization procedure is varied automatically so as to maintain the highest convergence rate at a preset accuracy.

Program for numerical analysis of the identifiability of kinetic model parameters. This program is run to calculate the sensitivity matrix for the responses of the model to variations of model parameters [16] and to factorize this matrix [14]. Next, an analysis is performed to single out the insignificant parameters, such as the rate constants of the rapid or slow reactions steps that are not to be determined precisely [16]; to single-out the constants that cannot be calculated alone, but only in combination with other parameters (so-called parameter complexes [11]); and to separate the parameters to be determined independently. For the latter parameters, (and, if necessary, for the parameter complexes), the determination error is calculated using the Fisher matrix [11, 16].

RESULTS AND DISCUSSION

The reaction between dihydrogen and palladium(II) acetate was studied using the above method of determining the amount of acetic acid resulting from the reduction of supported palladium(II) compounds [10]. Figure 1 plots the percentage yield of acetic acid (actual yield divided by theoretical yield), Y, as a function of the reaction time at two different temperatures (50 and 120°C) and two hydrogen partial pressures (1.0 and 0.052 atm). Clearly, the kinetics of

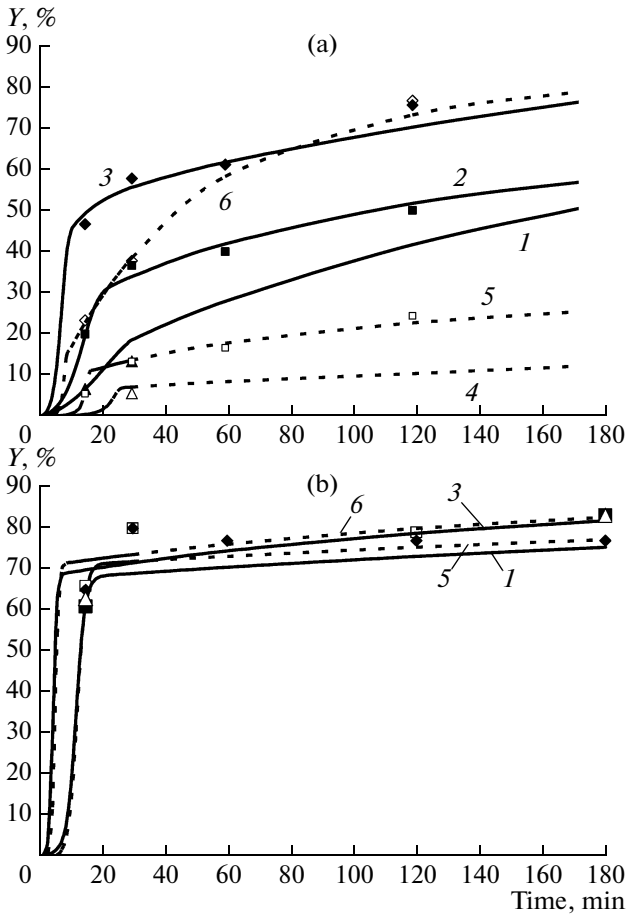

Fig. 1. Acetic acid formation kinetics at (a) 50 and (b) 120°C and different palladium acetate concentrations on the support and different hydrogen partial pressures: (*1*) 2% Pd, 1 atm; (*2*) 4% Pd, 1 atm; (*3*) 9.1% Pd, 1 atm; (*4*) 2% Pd, 0.052 atm; (*5*) 4% Pd, 0.052 atm; (*6*) 9.1% Pd, 0.052 atm. The points represent experimental data, and the lines represent the data calculated using the kinetic model.

this reaction is rather complicated and the averaged orders of the reaction with respect to the palladium and hydrogen concentrations are not integer. Furthermore, under certain reaction conditions (e.g., 4% Pd, 50°C), the kinetic curves are S-shaped and indicate an induction period. The induction period almost disappears as the palladium concentration and temperature are raised. Apparently, the induction period is shorter than 15 min under these conditions.

Similar kinetics were observed for the reduction of Pd(II) triphenylphosphine acetate complexes in solution [17]. The observed S-like shape of the kinetic curves is due to the autocatalytic action of the compounds of palladium in the low oxidation state and palladium hydride complexes in the reduction of the initial Pd(II) complexes [17]. However, there are significant distinctions between the reduction kinetics of Pd(II) in solution and that of Pd(II) on the surface. In solution, the Pd(II) compounds undergo comparatively slow reduction to palladium(I) and the latter is reduced rapidly to Pd(0). A radically different situation is observed on the support surface. In this case, the reduction rate falls markedly at $Y > 50\%$. It can be hypothesized that, on the support surface, the palladium(I) compounds result from the comparatively rapid reduction of palladium(II) acetate and are then reduced slowly to Pd(0). This is the likely reason why the maximum acetic acid yield attainable in 3 h for the sample containing 9.1% Pd at 50°C is $Y = 68\%$. As the reaction temperature is increased to 120 and 300°C, Y increases to 77 and ~100%, respectively.

The assumption that the Pd(I) compounds are reduced by hydrogen at a low rate and, as a consequence, accumulate on the support surface was fully verified by XPS studies. Figure 2 presents the X-ray photoelectron spectra of the samples containing 9.1% Pd that were reduced with hydrogen at 50 and 120°C for 30 and 180 min, respectively. The spectra show Pd(II), Pd(I), and Pd(0) peaks at binding energies of 338.2, 336.4, and 335.2 eV, close to those reported in the literature [18]. The Pd(II), Pd(I), and Pd(0) percentages in the total palladium content were determined by comparing the intensities of the corresponding Pd $3d_{5/2}$ peaks. The Pd(II), Pd(I), and Pd(0) percentages in the sample reduced at 50°C were found to be 25.3, 49.1, and 25.6%, respectively. Raising the reduction temperature to 120°C caused a decrease in the Pd(II) and Pd(I) contents and an increase in the Pd(0) content, just as was expected, and the corresponding percentages appeared to be 11.4, 34.8, and 53.8%.

From XPS data, we derived the theoretical amount of acetic acid that should result from the reaction: for 50 and 120°C, Y should be 50.2 and 71.0%. According to titration data, Y for these samples is 52.0 and 77.0%, respectively. Thus, the acetic acid yields measured by the two independent methods coincide within the experimental error.

All of the kinetic data (Fig. 1) and the XPS data for the samples reduced at the two different temperatures were used in the construction of a kinetic model.

The hypothetical mechanisms of the reaction included reaction step combinations corresponding to different states of the initial compounds and different intermediates, products, and conversion routes. About 100 hypotheses were considered. Using the procedure described in the experimental section, for each hypothesis we determined the goodness of fit between the model and the experimental data. Those descriptions were taken to be adequate for which the standard error did not exceed 7–10 rel. % and there were no systematic deviations between the calculated and experimental data in the entire ranges of experimental conditions (temperature, reaction time, hydrogen partial pressure, initial palladium(II) acetate concentration). When more than one hypothesis was adequate, we chose the simplest one, guided by the principle of simplicity (Occam's razor) [19].

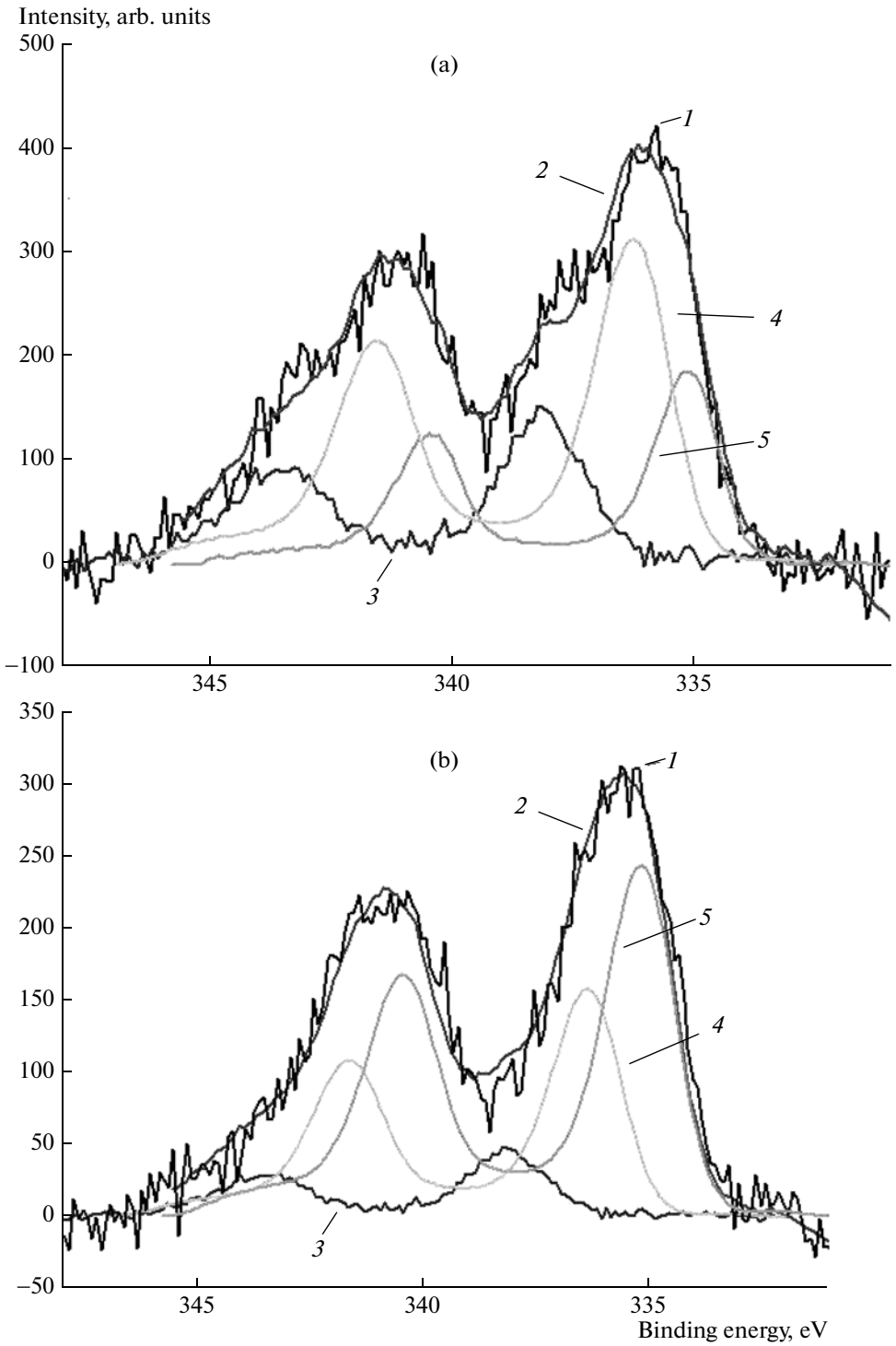

Fig. 2. (*1*) Observed X-ray photoelectron spectrum of palladium(II) acetate on the carbon support after reduction with hydrogen at (a) 50 and (b) 120°C. (*2–5*) Spectra obtained by deconvolution: (*2*) Pd(II) + Pd(I) + Pd(0), (*3*) Pd(II), (*4*) Pd(I), and (*5*) Pd(0).

It is quite obvious that the reduction of Pd(II) compounds is a multistep reaction both in solution and on the surface. Based on data available from the literature [17, 20] and on our experimental data, we suggested and analyzed the main reduction routes. These routes can conventionally be divided into seven groups each containing a number of reaction steps (Table 1).

The first group includes the reactions of palladium(II) acetate on the carbon surface before interaction with hydrogen.

Table 1. Rate constants of the reactions steps of the model at 50°C

Step no.	Chemical equation*	Group no.	Rate constant**	
			forward reaction	reverse reaction
1/2	**$Pd_3(OAc)_6 \leftrightarrow Pd_2(OAc)_4 + Pd(OAc)_2$**	1	3.17E+03	9.70E+08
3/4	**$Pd_2(OAc)_4 \leftrightarrow 2Pd(OAc)_2$**		1.16E+00	2.20E–01
5	**$Pd(OAc)_2 + H_2 \rightarrow Pd + 2HOAc$**	2	2.50E–03	
6	$Pd_2(OAc)_4 + H_2 \rightarrow Pd_2(OAc)_2 + 2HOAc$			
7	$Pd_2(OAc)_4 + H_2 \rightarrow Pd(OAc)_2 + Pd + 2HOAc$			
8	**$Pd_3(OAc)_6 + H_2 \rightarrow Pd_2(OAc)_2 + Pd(OAc)_2 + 2HOAc$**		2.29E–03	
9	$Pd_3(OAc)_6 + H_2 \rightarrow Pd_2(OAc)_4 + Pd + 2HOAc$			
10/11	**$2Pd_2(OAc)_2 \leftrightarrow Pd_4(OAc)_4$**		1.41E+01	2.96E+03
12/13	**$Pd + H_2 \leftrightarrow PdH_2$**	3	2.95E+08	7.42E+01
14/15	**$2Pd \leftrightarrow Pd_2$**		1.79E+10	
16/17	**$Pd_2 + H_2 \leftrightarrow Pd_2H_2$**		2.44E+06	
18	**$Pd(OAc)_2 + PdH_2 \rightarrow 2Pd + 2HOAc$**	4	8.63E+00	
19	$Pd(OAc)_2 + Pd_2H_2 \rightarrow Pd + Pd_2 + 2HOAc$			
20	**$Pd_2(OAc)_4 + PdH_2 \rightarrow Pd_2(OAc)_2 + Pd + 2HOAc$**		4.90E+04	
21	$Pd_2(OAc)_4 + PdH_2 \rightarrow Pd(OAc)_2 + 2Pd + 2HOAc$			
22	**$Pd_2(OAc)_4 + Pd_2H_2 \rightarrow Pd_2(OAc)_2 + Pd_2 + 2HOAc$**		5.63E+11	
23	$Pd_2(OAc)_4 + Pd_2H_2 \rightarrow Pd(OAc)_2 + Pd + Pd_2 + 2HOAc$			
24	**$Pd_3(OAc)_6 + PdH_2 \rightarrow Pd_2(OAc)_2 + Pd(OAc)_2 + Pd + 2HOAc$**		2.54E+02	
25	**$Pd_3(OAc)_6 + PdH_2 \rightarrow Pd_2(OAc)_4 + 2Pd + 2HOAc$**		1.65E+03	
26	$Pd_3(OAc)_6 + Pd_2H_2 \rightarrow Pd_2(OAc)_2 + Pd(OAc)_2 + Pd_2 + 2HOAc$			
27	**$Pd_3(OAc)_6 + Pd_2H_2 \rightarrow Pd_2(OAc)_4 + Pd + Pd_2 + 2HOAc$**		7.13E+05	
28	$Pd_2(OAc)_2 + H_2 \rightarrow 2Pd + 2HOAc$	5		
29	$Pd_4(OAc)_4 + H_2 \rightarrow Pd_2(OAc)_2 + 2Pd + 2HOAc$			
30	$Pd_2(OAc)_2 + PdH_2 \rightarrow 3Pd + 2HOAc$	6		
31	**$Pd_4(OAc)_4 + PdH_2 \rightarrow Pd_2(OAc)_2 + 3Pd + 2HOAc$**		2.12E+07	
32	$Pd_2(OAc)_2 + Pd_2H_2 \rightarrow Pd_2 + 2Pd + 2HOAc$			
33	$Pd_4(OAc)_4 + Pd_2H_2 \rightarrow Pd_2(OAc)_2 + Pd_2 + 2Pd + 2HOAc$			
34/35	**$Pd(OAc)_2 + Pd \leftrightarrow Pd_2(OAc)_2$**	7	4.09E+11	
36/37	**$Pd_2(OAc)_4 + Pd \leftrightarrow Pd_2(OAc)_2 + Pd(OAc)_2$**		2.09E+11	
38/39	**$Pd_3(OAc)_6 + Pd \leftrightarrow Pd_2(OAc)_2 + Pd_2(OAc)_4$**			9.42E+13

*The steps making a significant contribution to the overall reaction are set off in bold type.

**Units of measure: monomolecular reactions, min^{-1}; bimolecular reactions not involving hydrogen gas, g mol^{-1} min^{-1}; bimolecular reactions involving hydrogen gas, atm^{-1} min^{-1} (g is the weight of the support in grams). $E \pm n$ stands for $\times 10^{\pm n}$.

The IR spectroscopic study of the sample obtained by loading carbon with palladium(II) acetate without subsequent reduction with hydrogen (9.1% Pd) demonstrated that both the spectrum of the initial palladium(II) acetate, which is a trimer [21], and the spectrum of the supported acetate show two absorption bands due to the C–O stretching vibrations characteristic of bridging structures [22]. The position of the antisymmetric stretching band (1606 cm^{-1}) is almost unchanged by the supporting of the salt, while the symmetric stretching band shifts from 1429 to 1407 cm^{-1} and weakens. These data are evidence in favor of the assumption that the observed changes in the IR spectrum are due to the comparatively weak interaction between the palladium(II) acetate trimer and the support surface. Of course, it is not impossible that this interaction can initiate the reversible conversion of the trimer into dimeric and monomeric complexes stabilized by the carbon support, just as the solvent causes palladium(II) acetate, which is trimeric in

the crystalline state, to decompose to dimeric and monomeric species in solution [23].

Simulation of the reaction demonstrated that attempts to exclude the palladium acetate dimer and monomer (which differ in reactivity toward hydrogen from the trimer) from the reaction mechanism lead to an inadequate description. Inclusion of the tetramer into the reaction mechanism does not decrease the goodness of fit. It follows from the simulation data that, before reduction with hydrogen, the entire palladium(II) acetate is in the form of the trimer. The other assumptions lead to an inadequate description. Note that attempts to include reaction steps in which palladium(II) acetate changes its structure without changing its nuclearity, such as a change in the proportions of bridging and terminal acetate groups, dramatically reduce the goodness of fit. For this reason, reaction steps 1/2 and 3/4 were included in the first group.

The second group of reaction steps is made up by the noncatalytic reactions of different palladium acetate species with dihydrogen. The simplest step is the reaction between the palladium(II) acetate monomer with hydrogen yielding Pd(0) and acetic acid (step 5). This group also includes the reduction of the palladium(II) acetate dimer and trimer to Pd(0) and Pd(I) compounds (steps 6–9, 10/11). As a rule, the Pd(I) compounds are in dinuclear and tetranuclear forms [17, 24]. Hereafter, it is assumed that the reaction includes the interactions of palladium acetate trimers and dimers with hydrogen and with palladium hydrides or Pd(0) and that these interactions take place as follows. Part of the palladium of the initial complexes retains its initial oxidation state in the resulting compounds, and the other part undergoes reduction to Pd(I) or Pd(0) (steps 7–9, 21, 23–27, 29, 31, 33, 36/37, and 38/39). Inclusion of intermediate palladium(II) hydride–acetate complexes (whose formation was assumed for the reduction of palladium(II) acetate complexes in solution [17]) and the Pd(I) monomer and trimer into the reaction network does not improve the goodness of fit.

The third group consists of the reactions of compounds containing one or two Pd(0) atoms with hydrogen, which yield the corresponding hydrides (steps 12/13, 14/15, and 16/17). These hydrides can efficiently reduce palladium compounds, making the reaction autocatalytic [17].

The fourth group includes all reactions of the Pd(II) compounds with palladium hydrides, which result in the reduction of Pd(II) to Pd(I) and Pd(0). Specifically, the reduction of $Pd(OAc)_2$, $Pd_2(OAc)_4$, and $Pd_3(OAc)_6$ by the monomeric and dimeric palladium hydrides are meant here (steps 18–27).

The fifth and sixth groups include the interactions of Pd(I) compounds with hydrogen (steps 28 and 29) and palladium hydrides (steps 30–33), respectively.

The seventh group includes disproportionation reactions between a Pd(II) compound and Pd(0) yielding a Pd(I) compound, as in the case of palladium complexes in solution [17]. This group consists of steps 34/35, 36/37, and 38/39.

It was established that the reaction network presented in Table 1, which consists of 30 reactions, including 9 reversible ones, provides a good description for the observed kinetics. The error of this description does not exceed 5–7 rel. % for all reactions conditions examined. Figure 1 illustrates the good fit between the experimental data and the data calculated using this model.

Tables 1 and 2 list the numerical values of the rate constants for the reactions involved in the model at 50 and 120°C, respectively.

A detailed analysis of the results of the simulation using the above programs revealed the following. Reaction steps 1/2, 12/13, and 39 are very rapid and steps 3/4, 36, and 16 can be considered as relatively rapid. Since steps 6, 7, 9, 15, 17, 19, 21, 23, 26, 28–30, 32, 33, 35, 37, and 38 are very slow, they can be excluded from the reaction network without causing any significant changes in the result of simulation (this is true for the reaction steps whose rate constants are not included in Tables 1 and 2).

Because of the complexity of the reaction, the rate constants of most of its steps can be determined only in combination with other constants. The rate constants of only two reaction steps (24 and 25) can be calculated unambiguously (Table 1). These steps make the determining contribution to the reaction rate and palladium(II) acetate conversion, particularly in the region where the maximum acetic acid formation rate is observed.

At 120°C, steps 4, 11, and 18 are also very slow, like the above 17 steps. For this reason, it was possible to estimate the activation energy only for reaction steps 24 and 25 (Table 3).

The kinetic parameters thus determined enabled us to evaluate the roles of particular steps and palladium species in this complex reaction. The reaction begins with the slow reduction of the palladium(II) acetate trimer with dihydrogen (step 8), which yields the palladium(I) acetate dimer and palladium(II) acetate monomer. The reversible conversion of the palladium(II) trimer into the palladium(II) acetate dimer and monomer occurs simultaneously (steps 1/2 and 3/4).

The reduction of the palladium(II) acetate monomer to Pd(0) (step 5) ensures passage to the rapid phase of the overall reaction. The Pd and Pd_2 particles generated in step 14 turn comparatively rapidly into the hydrides PdH_2 (step 12) and Pd_2H_2 (step 16). Both hydrides reduce, more rapidly than dihydrogen, all forms of palladium(II) acetate—trimer (steps 24, 25, and 27), dimer (steps 20 and 22), and monomer (step 18)—to palladium(I) acetate or Pd(0). These reactions regenerate Pd(0), and this is among the fac-

Table 2. Rate constants of the reactions steps of the model at 120°C

Step no.	Chemical equation*	Group no.	Rate constant**	
			forward reaction	reverse reaction
1/2	**$Pd_3(OAc)_6 \leftrightarrow Pd_2(OAc)_4 + Pd(OAc)_2$**	1	3.36E+03	5.37E+15
3/4	**$Pd_2(OAc)_4 \leftrightarrow 2Pd(OAc)_2$**		1.16E+00	
5	**$Pd(OAc)_2 + H_2 \rightarrow Pd + 2HOAc$**	2	1.85E–02	
6	$Pd_2(OAc)_4 + H_2 \rightarrow Pd_2(OAc)_2 + 2HOAc$			
7	$Pd_2(OAc)_4 + H_2 \rightarrow Pd(OAc)_2 + Pd + 2HOAc$			
8	**$Pd_3(OAc)_6 + H_2 \rightarrow Pd_2(OAc)_2 + Pd(OAc)_2 + 2HOAc$**		2.29E–03	
9	$Pd_3(OAc)_6 + H_2 \rightarrow Pd_2(OAc)_4 + Pd + 2HOAc$			
10/11	**$2Pd_2(OAc)_2 \leftrightarrow Pd_4(OAc)_4$**		1.41E+01	
12/13	**$Pd + H_2 \leftrightarrow PdH_2$**	3	2.99E+09	2.03E+03
14/15	**$2Pd \leftrightarrow Pd_2$**		1.80E+10	
16/17	**$Pd_2 + H_2 \leftrightarrow Pd_2H_2$**		1.00E+07	
18	$Pd(OAc)_2 + PdH_2 \rightarrow 2Pd + 2HOAc$	4		
19	$Pd(OAc)_2 + Pd_2H_2 \rightarrow Pd + Pd_2 + 2HOAc$			
20	**$Pd_2(OAc)_4 + PdH_2 \rightarrow Pd_2(OAc)_2 + Pd + 2HOAc$**		1.06E+08	
21	$Pd_2(OAc)_4 + PdH_2 \rightarrow Pd(OAc)_2 + 2Pd + 2HOAc$			
22	**$Pd_2(OAc)_4 + Pd_2H_2 \rightarrow Pd_2(OAc)_2 + Pd_2 + 2HOAc$**		1.06E+12	
23	$Pd_2(OAc)_4 + Pd_2H_2 \rightarrow Pd(OAc)_2 + Pd + Pd_2 + 2HOAc$			
24	**$Pd_3(OAc)_6 + PdH_2 \rightarrow Pd_2(OAc)_2 + Pd(OAc)_2 + Pd + 2HOAc$**		4.99E+03	
25	**$Pd_3(OAc)_6 + PdH_2 \rightarrow Pd_2(OAc)_4 + 2Pd + 2HOAc$**		5.34E+03	
26	$Pd_3(OAc)_6 + Pd_2H_2 \rightarrow Pd_2(OAc)_2 + Pd(OAc)_2 + Pd_2 + 2HOAc$			
27	**$Pd_3(OAc)_6 + Pd_2H_2 \rightarrow Pd_2(OAc)_4 + Pd + Pd_2 + 2HOAc$**		8.41E+05	
28	$Pd_2(OAc)_2 + H_2 \rightarrow 2Pd + 2HOAc$	5		
29	$Pd_4(OAc)_4 + H_2 \rightarrow Pd_2(OAc)_2 + 2Pd + 2HOAc$			
30	$Pd_2(OAc)_2 + PdH_2 \rightarrow 3Pd + 2HOAc$	6		
31	**$Pd_4(OAc)_4 + PdH_2 \rightarrow Pd_2(OAc)_2 + 3Pd + 2HOAc$**		1.06E+09	
32	$Pd_2(OAc)_2 + Pd_2H_2 \rightarrow Pd_2 + 2Pd + 2HOAc$			
33	$Pd_4(OAc)_4 + Pd_2H_2 \rightarrow Pd_2(OAc)_2 + Pd_2 + 2Pd + 2HOAc$			
34/35	**$Pd(OAc)_2 + Pd \leftrightarrow Pd_2(OAc)_2$**	7	1.24E+18	
36/37	**$Pd_2(OAc)_4 + Pd \leftrightarrow Pd_2(OAc)_2 + Pd(OAc)_2$**		2.09E+11	
38/39	**$Pd_3(OAc)_6 + Pd \leftrightarrow Pd_2(OAc)_2 + Pd_2(OAc)_4$**			1.06E+16

*The steps making a significant contribution to the overall reaction are set off in bold type.

**Units of measure: monomolecular reactions, min^{-1}; bimolecular reactions not involving hydrogen gas, g mol^{-1} min^{-1}; bimolecular reactions involving hydrogen gas, atm^{-1} min^{-1} (g is the weight of the support in grams). $E \pm n$ stands for $\times 10^{\pm n}$.

tors responsible for the autocatalytic character of the reaction as a whole.

Note that the reduction of palladium(II) acetates, particularly that of the monomer and dimer, occurs not only under the action of dihydrogen or palladium hydrides, but also under the action of Pd(0) (steps 34 and 36). The latter results both from the reduction of palladium(II) acetates and from disproportionation (step 39). These steps also make a certain contribution to the autocatalytic character of the overall process.

As was noted above, unlike the palladium(II) acetates, the palladium(I) acetates are practically irreducible by dihydrogen and, at 120°C and below, are reduced slowly by PdH_2 (step 31). The active species in this reaction is the Pd(I) tetramer. Kinetic data demonstrate that the $Pd_2(OAc)_4$, $Pd_4(OAc)_4$, Pd, Pd_2, and Pd_2H_2 concentrations are low throughout the reaction; that is, they are short-lived intermediates.

The kinetic data obtained in this study make it possible to compare the mechanisms of Pd(II) reduction

in solution (for triphenylphosphine acetate complexes as an example) and on the support surface. The reaction is autocatalytic in both cases, but its mechanisms are somewhat different. In both cases, the initial palladium(II) compounds are reduced relatively slowly by dihydrogen to palladium(I) compounds. The trimeric, dimeric, and monomeric forms of palladium(II) acetate on the surface show different reactivities. Significant distinctions between the reaction in solution and the reaction on the surface are observed in the reduction of the palladium(I) compounds. In solution, the Pd(I) compounds are reduced by dihydrogen or palladium hydrides much more rapidly than the Pd(II) compounds. Just the reverse situation is observed on the surface, and palladium(I) reduction in this case is almost entirely due to palladium hydrides.

The resulting Pd(0) reacts with the initial Pd(II) both in solution and on the surface to yield Pd(I) compounds, which are then reduced to Pd(0). In both cases, the palladium hydrides reduce the initial Pd(II) compounds more rapidly than dihydrogen does. The difference is that, on the surface, the reduction of the monomeric form of Pd(II) to Pd(0) takes place (step 5), as is demonstrated by kinetic modeling. It is most likely that this process occurs without intermediate formation of Pd(I) compounds:

$$Pd(OAc)_2 + H_2 \longrightarrow PdH(OAc) + HOAc,$$

$$PdH(OAc) \longrightarrow Pd + HOAc.$$

For solutions of palladium(II) triphenylphosphine acetate complexes, the formation of monomeric species is not assumed [17].

Thus, if there were no step 5, Pd(0) accumulation on the surface would proceed much more slowly and this would lead to a significant decrease in the overall reaction rate.

The complexes of both Pd(II) and Pd(I) can react with various reductants, such as carbon monoxide, hydrogen, etc. [17, 20], and it was demonstrated that the redox properties of Pd(I) vary in a very wide range, depending on the nature of the ligands [20]. It can, therefore, be expected that the ratio of the rates of the Pd(II)-to-Pd(I) and Pd(I)-to-Pd(0) reductions by hydrogen will depend on the reaction conditions, on the composition of the complexes, and on the properties of the ligands (support). Our observation that Pd(I), as compared to Pd(II), is reduced less rapidly on the surface than in solutions of phosphine acetate complexes may have at least two causes. Firstly, the triphenylphosphine ligands present in these solutions stabilize the Pd(0) complexes [25] and can thereby favor Pd(I) reduction to Pd(0). Another possible cause is the interaction of the Pd(I) compounds with Pd(0) particles on the surface, which leads to a decrease in the reduction rate.

Thus, this kinetic study of the interaction between carbon-supported palladium(II) acetate and hydrogen demonstrated the possibility of obtaining materials with controllable proportions of different valence forms of palladium. This can be very helpful in the synthesis of catalysts with uncommon properties, primarily materials with a high Pd(I) content (5% and above).

Table 3. Rate constants and activation energies of the main steps of the reaction

Step no.	Rate constant, g mol^{-1} min^{-1}		E_a, kJ/mol
	50°C	120°C	
24	$2.54 \times 10^2 \pm 30\%$	$4.99 \times 10^3 \pm 30\%$	45 ± 8
25	$1.65 \times 10^3 \pm 30\%$	$5.34 \times 10^3 \pm 20\%$	18 ± 7

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