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Studying the Aluminum-Palladium Catalysts for Selective Acetylene Hydrogenation into Ethylene Prepared by Surface Self-Propagating Thermal Synthesis

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Abstract

Studies concerning supported aluminum-palladium catalysts obtained *via* surface self-propagating thermal synthesis (SSTS) for the selective liquid-phase hydrogenation of acetylene into ethylene in the presence of CO were performed. According to the results of catalytic testing, in the case of running the reaction at 60 °C the SSTS catalysts are inferior to the samples prepared in a conventional manner. At a temperature of 90 °C, the catalyst prepared *via* SSTS with using citric acid as a fuel additive is almost similar to the sample prepared via traditional method, in the catalytic properties thereof. According to the results obtained by EXAFS and XPS, the original SSTS catalysts contain palladium in oxidized and reduced forms, whose ratio depends on the nature and content of the fuel additive. It has been found that palladium oxide in SSTS catalysts can be quickly reduced under the reaction conditions to produce zero-valent Pd, which is indicated by the results of studying the SSTS catalysts before and after the reaction by means of EXAFS.

Key words: self-propagating surface thermal synthesis, liquid-phase hydrogenation of acetylene, EXAFS, XPS, Pd/Al_2O_3

INTRODUCTION

The reaction of acetylene liquid-phase hydrogenation to produce ethylene plays a key role in the transformation GTL (gas to liquid): process chain such as methane oxidative pyrolysis > acetylene > ethylene (important petrochemical raw materials) > oligomers (motor fuel). This technology was realized on a demonstration scale by Synfuels Int., Inc. (GTL technologies) [1, 2]. In the reaction of selective acetylene hydrogenation, the palladium catalysts applied onto various carriers are most active [2–8], thereby for increasing the selectivity level of the process with respect to acetylene one uses to introduce a gas phase modifier such as CO [6].

The activity and selectivity level of catalysts is to a considerable extent determined by the properties of the metal supported, namely by the levels of oxidation and dispersion, those depend on the method of preparing the catalysts. The traditional preparation method for palladium catalysts consists in the impregnation of different carriers with the solution of the precursor of an active component, with further drying, calcination and reduction. Under prolonged calcination and reduction at elevated temperature values the resulting particles of metallic palladium exhibit partial sintering, which can lead to reducing the selectivity level with respect to ethylene that according to literature data, depends on the dispersity level thereof [6]. Furthermore, the mentioned method of preparing the catalysts is rather laborious and energy-intensive. Modern selective hydrogenation catalysts should meet a set of certain requirements; one of those consists in the simplicity and low cost of producing the catalyst [8].

For the last time, in the preparation of catalysts there are widely used combustion methods, among those one should note the following: self-propagating high-temperature synthesis (SHS), dissolved precursors combustion synthesis of (DPCS), and various modifications of the DPCS such as sol-gel self-propagating combustion (SGSPC), impregnated carrier combustion (ICC) and applied impregnated active layer combustion (IALC) [9].

At this moment, in the literature there are several works devoted to the preparation of palladium hydrogenation catalysts by means of thermal synthesis *via* combustion in the flames [10].

The method of surface self-propagating thermal synthesis under our development (SSTS) [9] consists in the flameless combustion of the active component precursors (themselves or with fuel additives) applied on the carrier surface self-propagating over a carrier such as layer of granules, a block, or glass-fibre. As the result, in a short time (several minutes) one can prepare a sample with disperse and defective active components on the surface, and the synthesis temperature could be varied within the range of 300–1000 °C.

Thus, the SSTS allows one to perform rapid synthesis of metal oxide and metal catalysts on the carriers of different nature, varying the composition of the catalysts and parameters required for the synthesis over a wide range in order to obtain target physicochemical and catalytic properties. In this case, a relative environmental safety, low power consumption and manufacturability of the process determine the feasibility of this method.

The aim of this work consisted in a comparative study palladium catalysts applied onto γ-Al_2O_3 for the selective liquid phase hydrogenation of acetylene into ethylene in the presence of CO, both those prepared via conventional method (impregnation, drying, reduction), and those prepared *via* SSTS method. In the latter case, we studied an effect of fuel additives (glucose and citric acid) on SSTS process and on the structure and the catalytic properties of the resulting catalysts.

EXPERIMENTAL

Preparation of the catalysts

The samples of Pd/γ-Al_2O_3 were prepared by means of SSTS method. For comparison, a catalyst just the same in the gross composition was synthesized by means of a conventional method (impregnation, drying, and reduction in a flow of hydrogen at 200 °C for 3 h).

As the carrier, we have chosen γ-Al_2O_3 that represents spherical granules of about 2 mm in size (Ryazanskiy Co., Ryazan) with S_{BET} = 196 m^2/g, those were preliminary calcined at 580 °C for 6 h.

For the synthesis of the catalysts we used $Pd(NO_3)_2$ as the precursor of active component, and citric acid (CA) and glucose (Gl) as fuel additives (FA).

We prepared a series of samples whose palladium content amounted to 0.4 mass % as calculated for palladium metal.

Applying the palladium onto aluminum oxide surface was performed by means of impregnation (according to moisture capacity) by a solution of $Pd(NO_3)_2$ with a predetermined concentration that contained a certain amount of FA. A sample dried in air at 120 °C for 2 h, with palladium nitrate and FA applied were placed into a SSTS reactor [9]. Through the reactor passed a flow of heated air up to 80 °C (air flow rate 4.3 L/min) for 30 min. After setting a stabilized temperature value in the reactor (80 °C), we supplied voltage to a nichrome coil heater located at the bottom layer of the granules, to initiate a self-propagating exothermic reaction by the example of solid flameless combustion process. The initiation time amounted to about 30 s at a temperature of the coil heater about 750 °C. The temperature in the layer (at the front) was determined using a chromel-alumel thermocouple. The airflow rate in the course of the synthesis was equal to about 1.0 L/min. After passing the front of flameless combustion the air supply was stopped.

It should be noted that the samples prepared by means of the SSTS technique were not further exposed to any additional treatment in a hydrogen flow.

Catalytic testing

The catalytic testing of the prepared samples under investigation in the reaction of selective liquid-phase acetylene hydrogenation into ethylene (in the presence of CO enhancing the selectivity level with respect to ethylene) [2], was carried out in a shaking gradient-free flow-through temperature-controlled reactor under the following conditions: $P = 1$ atm, the volume of the gas mixture $V_{g/m} = 100$ mL/min, the frequency of shaking amounting to 6 s^{-1}; the mass of catalyst being equal to 0.30 g. The samples were previously grinded to obtain the fraction with a particle size <0.2 mm. As a solvent, we used *N*-methylpyrrolidone. The composition of the reaction gas mixture was as it follows (vol. %): C_2H_2 4, H_2 90, CO 2, He 4 (balance) [2]. One of the compartments of the reactor was loaded with a weighed sample portion, the other was loaded with 10 mL of the solvent, and thereafter the reactor was connected to a gas supply system. Further, in the course of heating the reactor using a MLW U4 water ultra thermostat (Germany) we began supplying the H_2 at a flow rate of about 60 mL/min. Upon reaching the target reactor temperature (90 °C) we fed the reaction mixture and started stirring. The catalyst was activated *via* passing the reaction mixture at 90 °C for 30 min. The catalytic characteristics thereof were determined at 60 and 90 °C. The total duration of the experiment was equal to 220 min. The sample was filtered from the solvent to place in a sealed plastic bag.

The composition of the initial reaction mixture and the mixture of reaction products was determined by means of a Chromos-1000 GC gas chromatograph equipped with a capillary column (25 m × 0.32 mm, NP − SiO_2, operating temperature 60 °C) and with a flame ionization detector. As a carrier gas we used nitrogen. Sampling frequency amounted to 35 min.

Within the experimental time, we obtained five chromatograms for the original reaction mixture and for the mixture after the reaction. In a similar manner as the authors of [2], from the areas of the corresponding peaks we calculated the acetylene conversion level (X, %) and selectivity level (S, %) with respect to ethylene and ethane. The selectivity level with respect to ethane for the reaction in the presence of CO was close to zero, thus the selectivity level with respect to oligomers (C_4) was determined as the difference between $100\,\% - S$ for ethylene. In addition, we obtained the dynamics for these variables from the catalyst testing time. For the comparative evaluation of characteristics for different samples under investigation we used the values thereof used within the range of the steady-state activity of the catalysts.

X-ray photoelectron spectroscopy

In order to determine the electronic state of the active component (palladium) we investigated original synthesized samples by means of XPS technique.

The registration of the spectra was performed using a KRATOS ES 300 XPS spectrometer (Kratos Analytical, UK). The spectra were registered in the mode of X-ray tube operation at 12 kV, 10 mA. As the primary radiation we used magnesium K_α line, the photon energy 1253.6 eV. The sample prepared (grinded) was fixed to the holder by means of a carbon tape. Survey spectra of the samples were registered within the binding energy range of 0–1100 eV with the energy pitch equal to 1 eV, at a constant energy transmittance of the analyzer HV = 50 eV. The vacuum level in the course of the analysis was equal to $1 \cdot 10^{-8}$ Torr.

The processing of the spectra was performed using XPSCalc and Easy Plot4 special software packages. The decomposition of lines in the narrow spectral areas inherent in the elements into individual components was performed after background subtraction according to Shirley method, in compliance with the minimum full half-width of the peaks equal to at least 1.6 eV.

EXAFS spectroscopy

The EXAFS spectra of the palladium K absorption edges for the catalysts under investigation were obtained by means of the EXAFS spectroscopy station of the Siberian Center for Synchrotron and Terahertz radiation (Institute of Nuclear Physics of the SB RAS, Novosibirsk). The spectra were obtained using synchrotron radiation at the electron energy value in the VEPP-3 storage ring equal to 2 GeV and at the current strength amounting to 70 mA using a split crystal Si (111) monochromator as in “transmission” and “fluorescence” modes with an increment of 2.5 eV. The spectra obtained were processed using a Viper software package via standard technique [11, 1]. In order to obtain quantum-chemical data required for calculating the structural parameters, we use a FEFF-7 software package [12]. Data concerning the structure of the compounds were taken from Inorganic Crystal Structure Database (ICSD) [13]. In order to determine the correction parameters in the course of the calculation of the coordination numbers, we additionally registered a reference spectrum of the palladium K absorption edge of palladium foil. The relative error in determining the distances was equal to 0.5 % that in determining the coordination numbers amounted to 10 %.

RESULTS AND DISCUSSION

Influence the nature and content of fuel additives upon the parameters of SSTS catalysts Pd/γ-Al_2O_3

The preparation of catalysts *via* SSTS, just as the preparation thereof *via* other combustion methods requires for using the FA in the case when the precursors of the active components are presented substances whose conversion into the active phase needs for heat consumption. Combustion characteristics are closely connected with the nature of FA.

In choosing FA, one should focus on the enthalpy of combustion thereof under standard conditions and the reactivity that provides appearing and maintaining a stable front of flameless solid-phase combustion in the course of SSTS and a complete decomposition of the precursor of an active component.

As mentioned above, as FA we have chosen citric acid (CA) and glucose (Gl).

Alongside with the nature of precursors (palladium and FA) and the ratio between them, as well as the flow rate of thermostating gas containing an oxidizer (oxygen), the important condition for SSTS, as it is in other variants of the combustion method, consists in the value of sample thermostating temperature. In our experiments, this value was equal to 80 °C.

We have determined the optimal ratio between FA and palladium nitrate which provides a stable SSTS front and complete decomposition of palladium nitrate (Table 1).

The dynamics of the combustion front in the course of the SSTS of catalysts with the composition of 0.4 % Pd/γ-Al_2O_3 in the presence of CA is presented in Fig. 1.

In this case, the SSTS oxidizer was presented by atmospheric oxygen and to a lesser extent by nitrogen oxides evolving in the course of the decomposition of the palladium nitrate applied. The observations of changing the speed of the front moving over the layer of alumina granules with precursors applied in the case of varying the air flow rate indicated that the rate-determining stage of the process is presented by supplying the oxygen to the reaction zone.

In the course of carrying out the SSTS it has been found that *via* varying the amount

TABLE 1

SSTS parameters for the synthesis of catalysts 0.4 % Pd/γ-Al_2O_3 (airflow rate in the synthesis 1.0 L/min)

Catalysts	Pd/FA ratio	SSTS parameters	
		Front velocity, mm/min	Front T_{max}, °C
0.4 % Pd/γAl_2O_3	Pd/CA (1 : 30)	3.9	590
0.4 % Pd/γ-Al_2O_3	Pd/CA (1 : 20)	5.5	540
0.4 % Pd/γ-Al_2O_3	Pd/Gl (1 : 15)	7.6	560
0.4 % Pd/γ-Al_2O_3	Pd/Gl (1 : 10)	8.4	460

Note. FA – fuel additive, CA – citric acid, Gl – glucose.

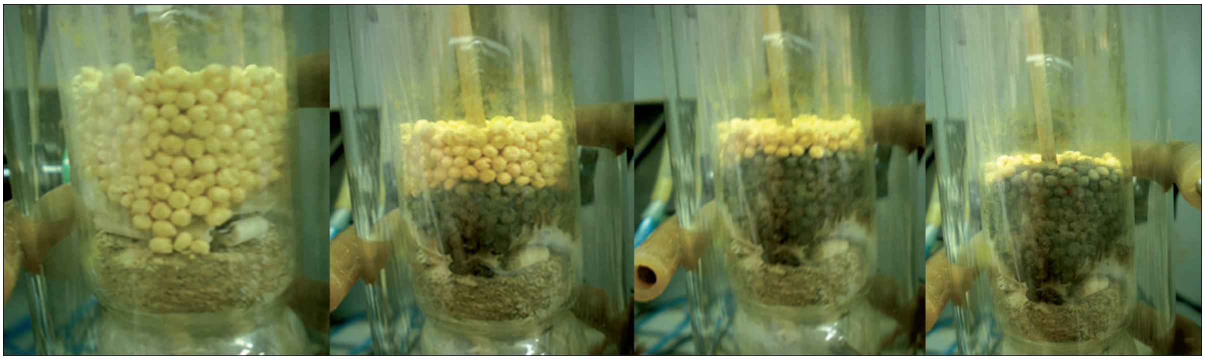

Fig. 1. Dynamics of the solid-phase combustion front propagation in the course of synthesizing the SSTS catalyst 0.4 % Pd/γ-Al_2O_3 (Pd/CA = 1 : 20). Under the catalyst bed there is ceramics with an electrical coil in order to initiate the process.

of glucose in the samples with Gl/Pd molar ratio < 10 the SSTS process either does not occur or the combustion front is interrupted. At the same time, the Gl/Pd ratio should not exceed 15, since a high viscosity of such solutions complicates the impregnation procedure.

When CA is used as the FA, there is flameless combustion front observed at CA/Pd ratio ≥ 20. However, this ratio should not exceed 30, because a high viscosity of such solutions also complicates the uniform impregnation of the carrier.

From data presented in Table 1 one can see that the temperature values developed in the front of the flameless combustion are considerable (from 460 to 590 °C). It should be noted that the use of the Gl as FA causes increasing the velocity of the combustion front propagation over the layer of the sample. The enthalpy of combustion for Gl is higher than that for CA (2802.04 and 1972.30 kJ/mol, respectively [14]); because of this the Gl/Pd ratio could be lower for occurring the SSTS as to compare with the value in the case of CA. It can be seen that increasing the amount of FA naturally leads to an increase in the temperature of the combustion front and to a decrease of the front propagation velocity over the layer of the sample from 8.4 to 3.9 mm/min at the sample layer height equal to 20 mm.

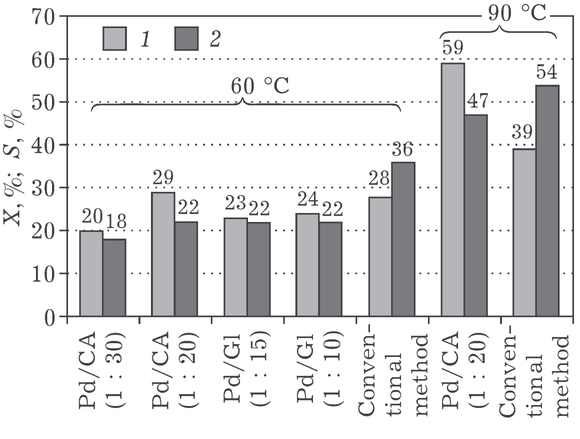

Fig. 2. Catalytic characteristics of catalysts 0.4 % Pd/γ-Al_2O_3, prepared by means of traditional method and *via* SSTS: *1* – ethylene selectivity level with respect to ethylene, *2* – acetylene conversion level (*X*).

According to [15], on condition that the enthalpy of combustion remains constant, the smaller the combustion time, the higher is the temperature of the synthesis. This could be connected with the fact that the heat loss within a short time interval is negligible and the major amount of the combustion heat is consumed for heating the products. Also, the combustion temperature is affected by the amount of gases evolved, because they dissipate the heat of synthesis to hinder the temperature from increasing. In turn, the amount of gases evolved is dependent on the contents of the FA.

Decreasing the front propagation rate is associated with the retardation of the oxygen diffusion from the air flow towards the combustion front, which is caused by an increase in the content of FA in the course of preparing the catalysts.

Catalytic testing of the samples prepared

Figure 2 demonstrates the catalytic properties of samples 0.4 % Pd/γ-Al_2O_3 in the reaction of liquid-phase acetylene hydrogenation into ethylene at the process temperature 60 and 90 °C.

It is seen that the catalyst 0.4 % Pd/γ-Al_2O_3 prepared by means of conventional method exhibit the selectivity level with respect to ethylene amounting to 28 % at a 36 % acetylene conversion level, which exceeds the values obtained for the SSTS catalysts. However, increasing the process temperature up to 90 °C results in noticeable changing the catalytic properties both of the SSTS catalyst, and of the sample prepared by means of traditional method. The SSTS sample with CA/Pd = 20 : 1 demonstrates a high selectivity level with respect to ethylene with a much lower conversion level of acetylene.

It has been established that in the case of using Gl as FA increasing the Gl content exerts no effect on the catalytic properties of SSTS samples. At the same time, increasing the content of CA results in lowering the conversion level of acetylene and lowering the selectivity level with respect to ethylene.

X-ray photoelectron spectroscopy

Figure 3 demonstrates the spectra of palladium Pd 3*d* level for the samples 0.4 % Pd/γ-Al_2O_3 with the decomposition of the spectra into components.

According to the authors of [16–24, 27, 29] the palladium applied onto Al_2O_3 could exist in the states Pd^0, PdO, PdO_2, and a combinations thereof. The binding energy values of the Pd 3*d* line for these compounds are observed within a narrow range and exhibit the following values: E_b (Pd $3d_{5/2}$) = 335.0–335.8 eV for Pd^0 [16–21, 29]; the authors of [21] observed for Pd^0 the E_b (Pd $3d_{5/2}$) = 336.1 eV; for PdO [16, 17, 21] E_b (Pd $3d_{5/2}$) being observed within the range of 336.6–337.4 and 336.1–336.8 eV [16, 23, 24, 27]; for PdO_2 E_b (Pd $3d_{5/2}$) = 337.4–339.3 eV [16, 17, 24, 27].

From the data presented in Fig. 3 it follows that the state of palladium in all the catalysts investigated corresponds palladium oxide PdO and metallic palladium Pd^0. All the samples of catalyst 0.4 % Pd/γ-Al_2O_3 with identical palladium content and characteristics of the carriers differ in the method of preparation. So, the first of them (see Fig. 3, *a*) was obtained by means of reduction in hydrogen, because of this the palladium in the surface layer of the sample is predominantly in the metallic state. The presence of components corresponding to the oxidized palladium could be explained by the oxidation of the surface of metal particles in the course of moving the catalyst from the reduction reactor to the unit for registering the XPS spectra.

The SSTS sample 0.4 % Pd/γ-Al_2O_3 (Pd/CA = 1 : 30) contains the palladium in the form of oxide (E_b = 337.1 eV) and metal nanoparticles (E_b = 335.5 eV) (see Fig. 3, *b*). The observed shift of the binding energy in small metal clusters as to compare with bulk metal could be caused either by the effect of the relaxation of a hole formed in the course of photoemission (the effect of the final state), or by any deficiency in the electron density within small clusters (the effect of the initial state) [25–30].

The percentage of palladium in oxidized and metallic forms on the catalyst surface is almost the same.

The SSTS sample with Pd/CA = 1 : 20 (see Fig. 3, *c*), exhibits the content of CA to be lower, but the ratio of Pd/PdO therein is about the same as that is in the sample 0.4 % Pd/γ-Al_2O_3 with Pd/CA = 1 : 30. In addition, the spectral component that is responsible for the metallic state is slightly shifted toward higher values of the binding energy (E_b = 335.4 eV) as compared to the data for the bulk metal (E_b = 335.0–335.2 eV), which could indicate a small particle size of palladium.

The SSTS sample 0.4 % Pd/γ-Al_2O_3 with Pd/Gl = 1 : 15 (see Fig. 3, *d*) exhibits the palladium to be in the reduced and oxidized forms. The peak at 335.6 eV formally corresponds to metallic clusters, whereas the component at 337.5 eV has an increased binding energy in comparison with the value inherent in palladium oxide. However, most likely, this peak just corresponds to palladium oxide PdO, whereas the positive shift could be explained, firstly, by an error of spectra decomposition under insufficient statistics (the intensity of palladium line is very low) and, secondly, by possible manifestation of an inhomogeneous distribution of the surface potential (differential charging), which often occurs in the course of studying highly dielectric materials [30]. In any case,

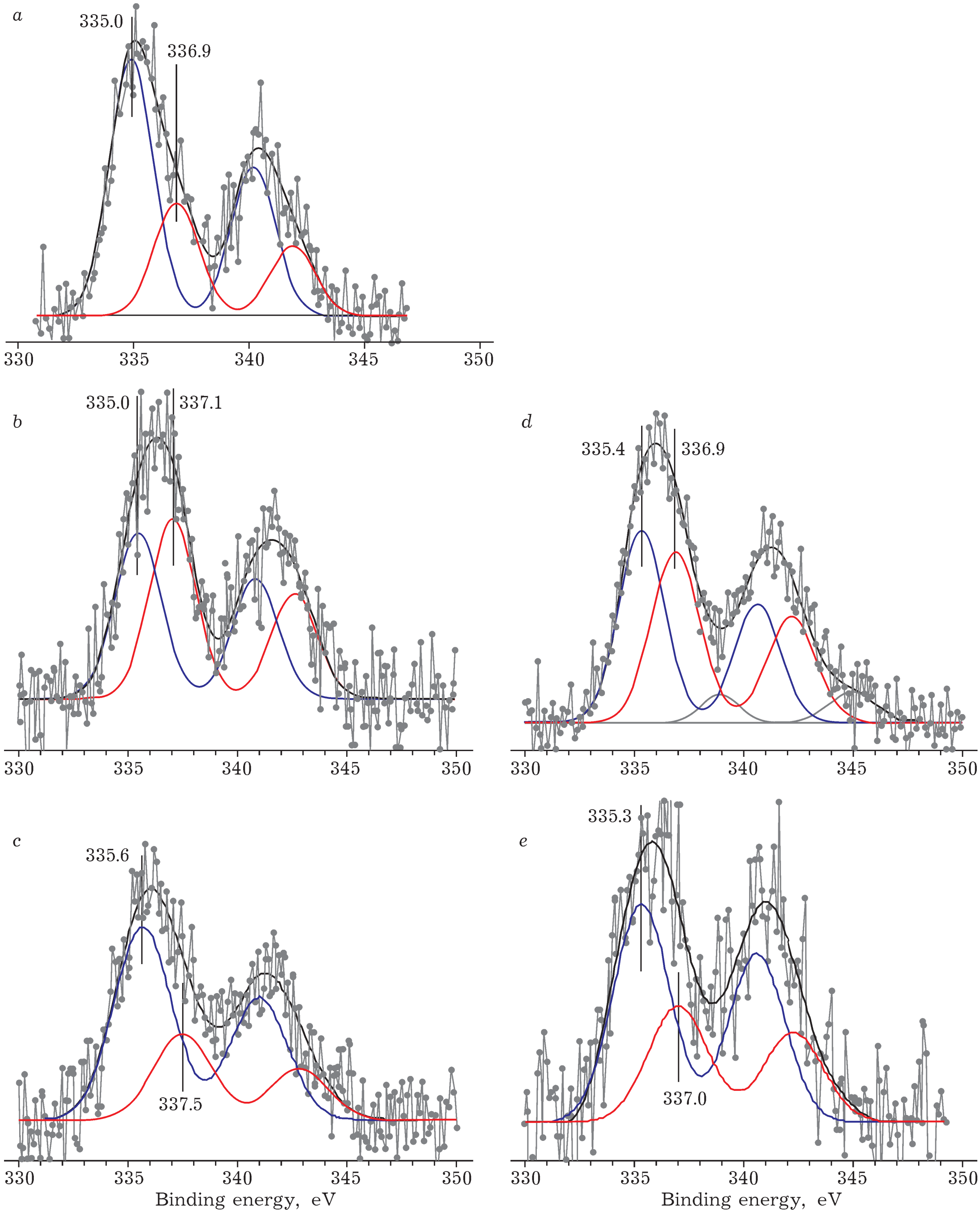

Fig. 3. Pd 3*d* spectra for various catalysts 0.4 % Pd/γ-Al_2O_3: *a* – prepared by means of traditional method; *b*–*e* – obtained *via* SSTS at ratio values Pd/CA = 1 : 30 (*b*), Pd/CA = 1 : 20 (*c*), Pd/Gl = 1 : 15 (*d*), Pd/Gl = 1 : 10 (*e*).

the palladium in this catalyst, to all appearance, is predominantly in the metallic state.

As far as the SSTS sample 0.4 % Pd/γ-Al_2O_3 with Pd/Gl= 1 : 10 is concerned (see Fig. 3, *d*), the palladium is present therein in the form of metal particles (E_b = 335.3 eV) and oxide particles PdO (E_b = 337.0 eV). It can be seen that the fraction of palladium oxide is lower, *i. e.*, the palladium is predominantly in the reduced state.

However, taking into account the value of signal/noise ratio in the spectra of the samples with Pd/Gl = 1 : 15 and 1 : 10, a small contribution of the oxide components in Pd 3*d* line should be asserted with caution.

Thus, according to XPS data, the original SSTS samples obtained using Gl as the FA exhibit the fraction of metallic palladium in the surface layers of the particles to be significantly higher as compared to the SSTS samples, where FA is used as CA, which could be associated with a higher reducing ability of the Gl.

EXAFS spectroscopy

In order to obtain structural information concerning the state of palladium catalysts, we registered EXAFS spectra for the *K* absorption edges of palladium samples 0.4 % Pd/γ-Al_2O_3.

In the course of the studies we also registered an EXAFS spectrum for the *K* absorption edge of palladium contained in the sample prepared *via* traditional method, too. According to the information obtained, the active component is present in the form of metal, since the spectrum exhibit Pd–Pd distance equal to 2.75 Å only, with the coordination amounting to 3.8 and the Debye–Waller factor value equal to $69 \cdot 10^{-4}$ Å^2.

Figure 4 demonstrates the curves of radial atomic distribution (RAD) around the palladium atoms for the samples 0.4 % Pd/γ-Al_2O_3, prepared by means of SSTS using different FA (Gl, CA) and with different Pd/FA ratio values. The spectra of palladium *K* absorption edge for these samples were removed before testing thereof in the reaction of liquid-phase acetylene hydrogenation.

It is seen that prior to the reaction the samples contain the active component mostly in the form of palladium oxide (Pd–O distance being equal to 2.01 Å, Pd–Pd distance amounting to 3.04 and 3.46 Å, which is consistent with the structure of PdO), whereas a small portion of Pd is in the form of palladium metal (Pd–Pd distance being equal to 2.75 Å, which corresponds to the first coordination sphere of metallic *fcc* Pd) (see Fig. 4) [13, 29]. Basing on the

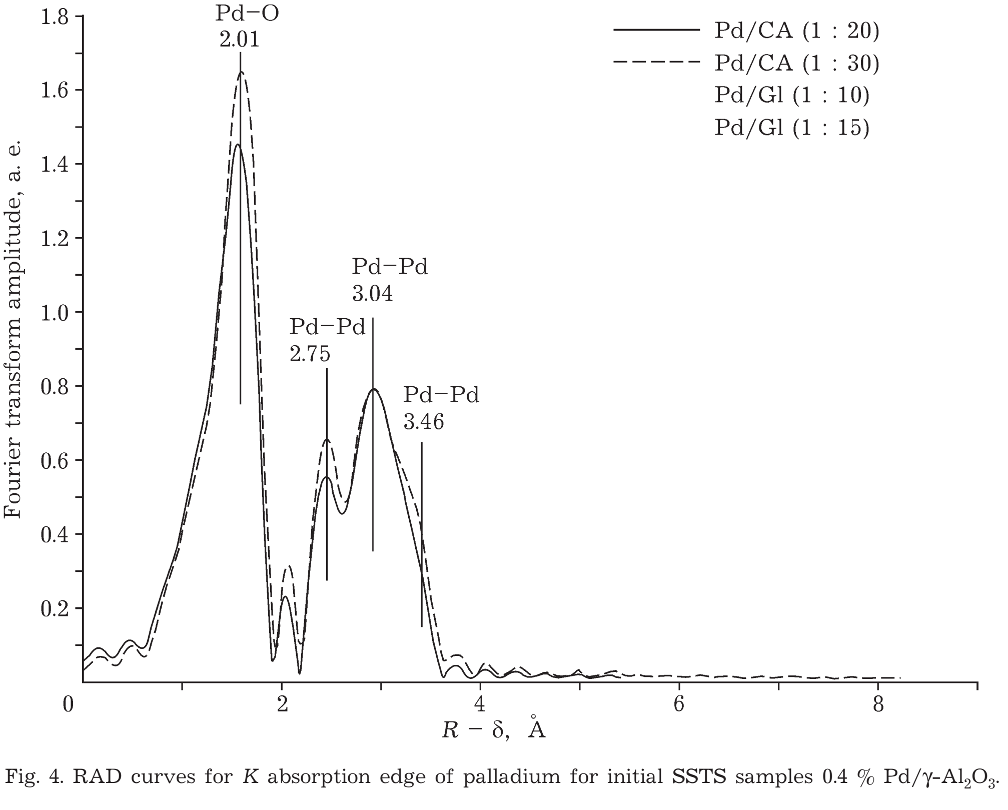

Fig. 4. RAD curves for *K* absorption edge of palladium for initial SSTS samples 0.4 % Pd/γ-Al_2O_3.

TABLE 2

Estimating the number of Pd^0 and Pd^{2+} on the basis of the coordination numbers (CN) PdO for original samples

Pd/FA ratio	CN for Pd–O	Pd^{2+}, %	Pd^0, %
Pd/CA (1 : 20)	2.38	60	40
Pd/CA (1 : 30)	2.58	65	35
Pd/Gl (1 : 10)	2.26	57	43
Pd/Gl (1 : 15)	2.67	67	33

coordination number values for Pd–O distance obtained *via* simulation we calculated relative Pd^0 и Pd^{2+} amounts contained in these catalysts (Table 2).

According to EXAFS data, the samples obtained at a high FA content, the proportion of the oxide phase is higher. This could be caused by the fact that increasing the content of the FA the results in increasing the rate of palladium oxidation by gaseous products formed and by atmospheric oxygen, as well as a longer time of cooling the sample up to a room temperature. According to XPS data, in the case of using the Gl as FA the surface layer of palladium particles is reduced to a greater extent than it is with the use of CA. However, there is no contradiction, since the EXAFS method allows one to determine the state of palladium in the whole bulk of the particle, whereas the XPS can determine this feature for the surface layer only. Palladium in the metallic (zero-valent) state, according to the data of modelling is disordered to a considerable extent: the samples obtained with the use of FA exhibit the Debye–Waller factor within the range of $(108–189) \cdot 10^{-4}$ Å^2, which is higher as to compared with that for a sample prepared with the use of the conventional method. The coordination numbers according the Pd–Pd distance are low to amount to 1.5–1.8.

Figure 5 demonstrates the EXAFS spectra of the palladium *K* absorption edge for the samples under investigation after testing them in the reaction of liquid-phase acetylene hydrogenation.

It is known that palladium oxide can be reduced by hydrogen at relatively low temperature values, for example at a room temperature [31, 32]. It is unsurprising that SSTS catalysts containing substantial amounts of PdO can be reduced by the reaction mixture to produce palladium metal in the course of the reaction (the XRD curves exhibit ~ 2.78 Å peak corresponding to the distance in the Pd–Pd metal).

Preliminary experiments demonstrated that already after the activation at 90 °C for 30 min, the palladium becomes completely reduced. Increasing the Pd–Pd distance (2.78 instead of 2.75 Å in the bulk metal), to all appearance, could be caused by the presence of impurities in the bulk palladium particles [33].

In order to verify the idea concerning the introduction of impurities into the active com-

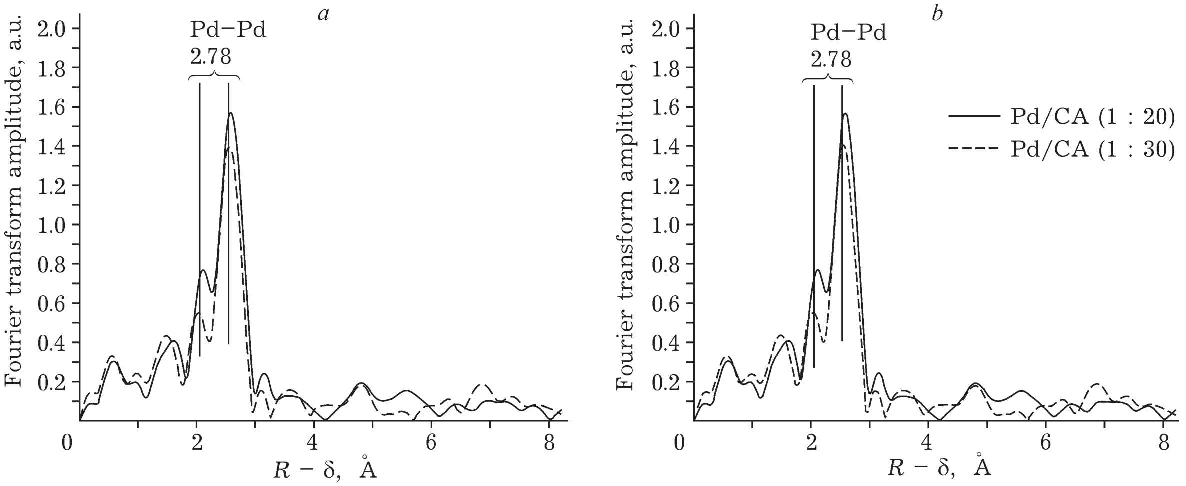

Fig. 5. RAD curves for *K* absorption edge of palladium for SSTS samples 0.4 % Pd/γ-Al_2O_3, prepared using citric acid (*a*) and glucose (*b*) after the reaction.

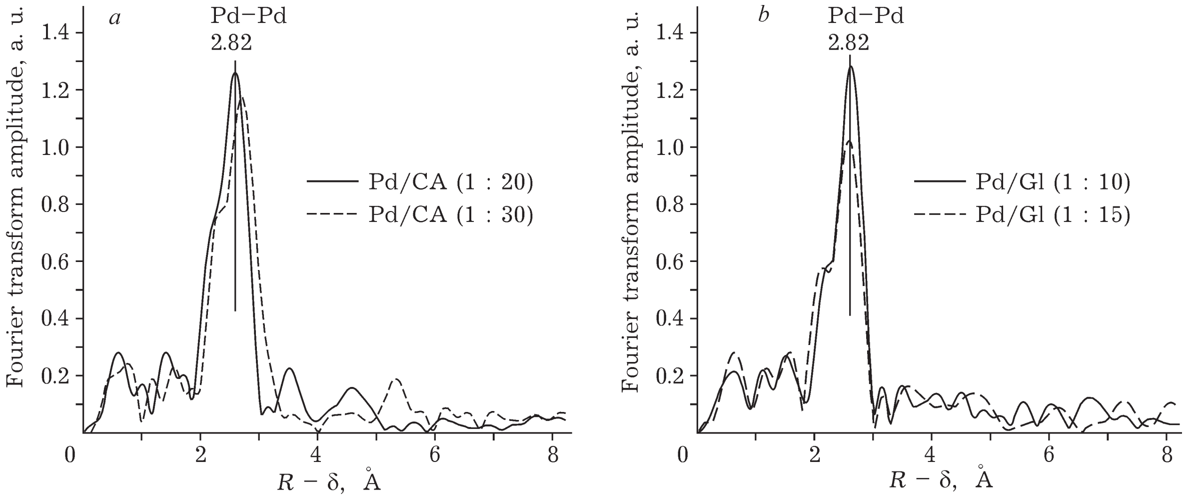

Fig. 6. RAD curves for *K* absorption edge of palladium for SSTS samples 0.4 % Pd/γ-Al_2O_3, prepared using citric acid (*a*) and glucose (*b*) and calcined in flowing helium at 140 °C.

ponent, the samples after testing in the hydrogenation reaction were dried in a flow of helium (60 mL/min) at 60 °C for 40 h. The samples were then calcined in flowing helium (60 mL/min) at 140 °C for 4 h. For the calcined samples we registered EXAFS spectra, too (Fig. 6).

After the calcination in a flow of helium at 140 °C the palladium in the sample remains in the metallic state, but the Pd–Pd distance exhibits an increase up to 2.82 Å. The peak located on the $R - \delta$ scale at a distance of 1.5 Å might correspond either to Pd–O bond or to Pd–C bond. The peaks at the distances of 3–5 Å (on the $R - \delta$ scale) do not correspond to the distances between the coordination spheres in the palladium foil, to all appearance, because of a very profound distortion of the structure of the metal supported.

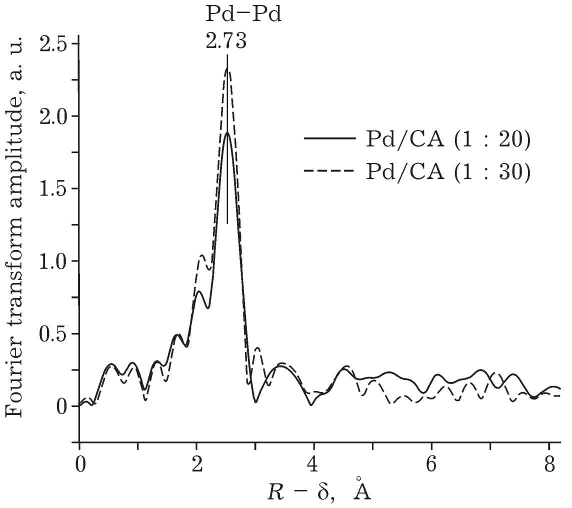

Fig. 7. RAD curves for *K* absorption edge of palladium for SSTS samples 0.4 % Pd/γ-Al_2O_3 obtained by using citric acid and calcined in flowing helium at 250 °C.

To all appearance, removing the impurities from the palladium particles requires for a higher temperature of thermal desorption. With this purpose, the samples after testing in the hydrogenation reaction were dried in a flow of helium (60 mL/min) at 60 °C during 40 h and further they were calcined in flowing helium (60 mL/min) at 250 °C during 4 h. For these samples, we registered EXAFS spectra, too (Fig. 7).

After the calcination in flowing helium at 250 °C, the palladium in samples is in the metallic state, whereas the Pd–Pd distance exhibits a decrease from 2.82 to 2.73 Å, which corresponds to the *fcc* lattice of the metallic palladium. This might indicate the fact that the impurities are removed from the bulk of palladium particles.

CONCLUSION

Influence of the nature of fuel additives upon the parameters of self-propagating surface thermal synthesis such as front propagation velocity and maximum front temperature was studied. It has been demonstrated that depending on the conditions of performing the SSTS the front propagation velocity ranges within 3.9–8.4 mm/min, whereas the maximum temperature values range from 460 to 590 °C. The nature of the fuel additive affects the temperature of the solid phase combustion front and the reduction level of palladium.

Using an express SSPTS method we obtained promising supported aluminum-palladium catalysts for the reaction of selective liquid-phase acetylene hydrogenation in the presence of CO. The selectivity level with respect to ethylene at 60 °C for SSTS samples prepared using citric acid as a fuel additive is lower as to compare with that for the sample with the same content of the catalyst prepared via traditional method. It is demonstrated that at a higher process temperature (90 °C), the catalyst obtained by means of SSTS using citric acid is almost similar in the characteristics thereof to a catalyst produced by the conventional method.

By means of XPS and EXAFS methods, we determined electronic and structural state of supported palladium. It has been demonstrated that the catalysts contain Pd^0 and PdO in different proportions depending on the preparation conditions. According to the results of EXAFS and XPS, the original SSTS catalysts contain palladium in oxidized and reduced forms, whose ratio depends on the nature and content of the fuel additive.

It has been found that palladium oxide in SSTS catalysts can be rapidly reduced under the reaction conditions to produce zero-valent Pd. This is confirmed by the results of studying the SSTS catalysts before and after the reaction with the use of EXAFS technique.

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