Effect of Preparation Conditions on Characteristics of Modified Palladium Catalysts of Liquid-Phase Acetylene Hydrogenation

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Abstract

The effect of the reduction period in hydrogen of Pd/Sibunit and Pd–M/Sibunit (M: Ga, Zn, Ag) catalyst, as well as the nature of palladium and zinc precursors on properties of samples in the of liquid-phase hydrogenation reaction of acetylene into ethylene was investigated. It was found that the introduction of the second metal (Ga, Zn, and Ag) into the Pd catalyst prevented sintering of the active component during reductive thermal treatment resulting in the reduction period does not affect the activity and selectivity of the modified catalysts, unlike an unmodified Pd/Sibunit sample. For the Pd–Zn/Sibunit sample, it was demonstrated that modification with zinc led to a change in the nature of catalytic active sites and an increase in their number, regardless the nature of metal precursors; herewith, the Pd–Zn/Sibunit system synthesized from solutions of palladium nitrate and zinc nitrate is distinguished by a higher activity and selectivity.

Key words: liquid-phase hydrogenation of acetylene, palladium catalyst, modification, Pd–Ga, Pd–Zn, Pd–Ag

INTRODUCTION

Ethylene is an important raw material for industrial organic synthesis. Ethylene traditionally obtainable by pyrolysis of liquid oil distillates or lower saturated hydrocarbons contains acetylene impurities that are capable of irreversibly deactivating catalysts of its subsequent processing. In this regard, purification of ethylene from concomitant acetylene by gas-phase catalytic hydrogenation is a necessary technological process [1, 2]. Another promising preparation method of ethylene is the technology of an American Synfuels International, Inc. Company that includes the following processes: the preparation of acetylene by oxidative pyrolysis of natural gas, C_2H_2 adsorption with a selective solvent-adsorbent and subsequent selective liquid-phase hydrogenation of acetylene into ethylene. In this case, hydrogenation is carried out in the solvent medium, which en-

sures the safety of this highly exothermic process ($\Delta H = -174.5$ kJ/mol) and contributes to selectivity improvement by ethylene [3–5].

As catalysts for acetylene hydrogenation, applied palladium, including modified with the second metal (more often, IB, IIB or IIIA subgroup) are used [4, 6]. Catalytic systems based on bimetal compositions are distinguished by a high activity, selectivity, as well as resistance to deactivation [1, 7], which according to the literature data, is conditioned by the formation in these systems of bimetal phases, and accordingly, by the manifestation of the geometric («dilution» with a modifier of the neighbouring Pd atoms) and electronic (changes in the electronic state of Pd) components of the interaction of palladium and element modifier [8].

The composition and structure of the active component of the catalyst, size of applied particles, as well as the degree of manifestation of the modifying effect are heavily de-

pendent on the sample preparation method. In particular, catalyst treatment time at elevated temperatures (sintering or reduction processes), the nature of the active component precursor, molar ratio of palladium to the modifier and other factors have an effect [9]. In this regard, the work purpose was the effect assessment of the reductive thermal treatment of Pd−M/Sibunit (M: Ga, Zn, Ag) catalysts and nature of palladium precursors and modifier (on the example of Pd?Zn/Sibunit system) on their catalytic characteristics in the liquid-phase hydrogenation reaction of acetylene into ethylene. N-methyl-2-pyrrolidone that possesses a high absorptive capacity for acetylene was used as a solvent [4, 5].

EXPERIMENTAL

Catalyst preparation

Carbon compositional material Sibunit (technical specifications TU 38 41540−95, S_{BET} ~ 336 m^2/g, fraction of 0.07−0.09 mm pre-treated with a solution of 5 % HNO_3 for the purpose of increasing the sorption interaction of the active component with the carrier and reducing the hydrophobicity of the material) was used as a carrier. Samples were prepared by the carrier impregnation by moisture capacity with water solutions simultaneously containing palladium compounds ($Pd(NO_3)_2$) and one from metal modifiers ($Ga(NO_3)_3$, $Zn(NO_3)_2$ or $AgNO_3$). In case of an unmodified Pd/Sibunit sample, the impregnating solution consisted of $Pd(NO_3)_2$ only. The resulting catalysts were dried for 2 h at 120 °C (for Pd−Ag drying was conducted for 12 h at 25 °C). The samples were further reduced in a current of hydrogen (volumetric flow rate of H_2 is 60 mL/min) at 500 °C (for Pd−Ag, the temperature of reduction was 300 °C). The thermal treatment time in hydrogen was varied (1, 3, 5 h). Additionally, Pd/Sibunit and Pd−Zn/Sibunit samples that were dried for 2 h at 120 °C and reduced in hydrogen for 3 h at 500 °C were prepared from $[Pd(NH_3)_4](CH_3COO)_2$ and $[Zn(NH_3)_4](CH_3COO)_2$ following the same technique. All the resulting catalysts contained 0.50 % mass palladium. The modifier content corresponded to a molar ratio 1 : 1 of Pd/M.

High resolution transmission electron microscopy (HRTEM)

The structure of samples was studied by the TEM method (JEM 2010, JEOL, Japan with an accelerating voltage of 200 kV and a limiting resolution of 0.14 nm). Catalysts were grinded in ethanol using an UZD-1Uch2 sonicator and the suspension was applied on carbon substrates attached to copper meshes. This allowed reaching the uniform distribution of particles along the substrate surface. The linear calibration at measurements of the particle diameter was performed according to the crystal lattice of the gold particles. Herewith, the metering error of linear dimensions on electron microscope images did not exceed 0.02 nm. Images were recorded using a Soft Imaging System (Germany) CCD matrix. The particle-size distribution of the applied metal particles and their mean diameter were assessed from the resulting microscopic data.

Catalytic tests

Trials of the resulting samples were carried out in a laboratory the setup for liquid-phase hydrogenation of acetylene in UZD-1UCh2 sonicator flow thermostated reactor [10] at a temperature of 55 °C and atmospheric pressure. In experiments on palladium and zinc precursors variation, the temperature was changed from 35 to 50 °C with a step of 5 °C. The catalyst in the amount of 20 mg was introduced into a metal reactor, 8.0 mL of a solvent (N-methyl-2-pyrrolidone) was poured in and a gas mixture that included 4 vol. % C_2H_2 and 96 vol. % H_2 (consumption of 100 mL/min) was supplied. Measurements were performed at intensive shaking − the oscillation frequency of the reactor amounted to 7−8 s^{-1}. The current composition of the reaction mixture consisting of unreacted acetylene and major products of the hydrogenation reaction that were ethane, ethylene and C_{4+} oligomers was controlled by the gas-solid chromatography (GSC) using a Chromos GC-1000 chromatograph (Russia) equipped with a capillary column (SP − SiO_2) and flame ionization detector (carrier gas − nitrogen). The time of a single experiment was 220 min, which
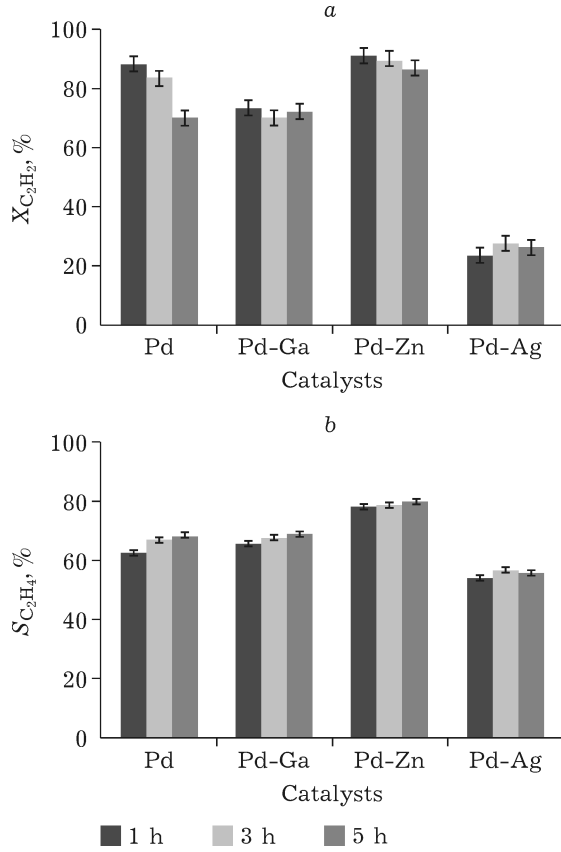
Fig. 1. Acetylene conversion degree (*a*) and selectivity for ethylene (*b*) for Pd/Sibunit and Pd−M/Sibunit (M: Ga, Zn, Ag) catalysts prepared from nitrates at different times of thermal treatment in H_2 (T_{react} = 55 °C).

allowed determining the values of the studied characteristics of catalysts within the scope of their stationary activity.

The degree of acetylene conversion ($X_{C_2H_2}$, %), selectivity for ethylene ($S_{C_2H_4}$) and activity (W_{cat}) in terms of per gram of catalyst were calculated according to according to the areas of the corresponding peaks in the chromatograms, using normalization methods:

$$X_{C_2H_2} = \frac{Z_{C_2H_6} + Z_{C_2H_2} + \Sigma Z_{C_{4+}}}{Z_{C_2H_6} + Z_{C_2H_2} + Z_{C_2H_4} + \Sigma Z_{C_{4+}}} \cdot 100\ \%$$

$$S_{C_2H_4} = \frac{Z_{C_2H_4}}{Z_{C_2H_6} + Z_{C_2H_4} + \Sigma Z_{C_{4+}}} \cdot 100\ \%$$

where Z is content of C_2H_4 and the reaction products, mass %;

$$W_{cat} = \frac{V_{mix} C_0 X_{C_2H_2}}{m_{cat}} \cdot 100\ \%$$

where V_{mix} is volume rate of supply of the reaction mixture, mL/min; C_0 is initial concentration of C_2H_2 in the flow of the reaction mixture, mL C_2H_2/mL gas mixture; m_{cat} is mass of catalyst sample, g.

The characteristics listed are well reproduced both when repeating an individual experiment and repeated preparing samples of the same type; appropriate variation coefficients did not exceed 5 %.

RESULTS AND DISCUSSION

Duration effect of reductive thermal treatment

According to the data obtained, the duration of reductive thermal treatment for Pd/Sibunit and Pd−M/Sibunit (M: Ga, Zn, Ag) of catalyst have little impact on properties of the samples modified. Distinctions in the values of the transformation degree of acetylene for selectively for Pd−M/Sibunit reduced during 1, 3 and 5 h are insignificant. Along with that, reduction of the applied monometallic Pd sample during 5 h led to significant reducing $X_{C_2H_2}$, which is supposedly associated with sintering palladium particles during reductive thermal treatment (Fig. 1) [11].

To verify the hypothesis put forward samples reduced during 3 h were studied by a method of HRTEM. According to the resulting microscopic data, carbon carrier particles as agglomerates with the size distribution from 100 nm to a few dozen micrometres are present in all catalysts, and the applied component is evenly distributed along the carrier and exists in the form of spherical form particles. Herewith, the modified catalysts are characterized by much smaller sizes of metal particles (in 2

TABLE 1

Diameter of the supported particles in Pd/Sibunit and Pd−M/Sibunit (Pd/M = 1 : 1) catalysts reduced in H_2 for 3 h at 500 °C

Catalysts	d_{av}, nm	d_{min}, nm	d_{max}, nm
Pd/Sibunit	4.0	1.1	10.9
Pd−Ga/Sibunit	2.0	1.2	4.0
Pd−Zn/Sibunit	1.6	1.1	2.7
Pd−Ag/Sibunit	1.7	0.6	3.5

and more times) in comparison with the reference sample Pd/Sibunit (Table 1).

The regularity detected proves that modifying a Pd catalyst with gallium, zinc, as well as silver prevents the formation of large particles in the preparation process of catalysts obstructing in such a way sintering of the active component. Therefore, the observed constancy of catalytic characteristics of modified catalysts at an increase in the reductive thermal treatment time in hydrogen is associated with stabilization of palladium dispersity by the introduced modifier. Additionally, as can be seen from data of Table 1, the modification significantly (over 3.5 times) narrows down the applied particle size distribution. Unfortunately, data available do not enable to judge of the reasons for the observed effect, at the same time, the literature lacks the explanation of the mechanism of an increase in dispersity of applied palladium when introducing a modifier [12−14]. It is likely that at drying and subsequent reductive treatment of oxynitrates formed and then and metal particles of modifiers are "traps" that interact with small particles of palladium formed under these conditions, which hinders their sintering.

As can be seen (see Fig. 1), modification of Pd catalysts with gallium and especially with silver does not lead to improving their characteristics. On contrary, modification with zinc drives a reliable increase of $S_{C_2H_4}$ (by ~20 rel. %) at almost unchanged $X_{C_2H_2}$ value, due to which the major attention was further focused on precisely Zn-containing catalysts.

Effect of the nature of precursors

The effect of the nature of palladium precursors was studied by comparing catalytic characteristics ($X_{C_2H_2}$ and $S_{C_2H_4}$) of Pd/Sibunit and Pd−Zn/Sibunit samples obtained (at other identical conditions) from nitrates and ammonia complexes in a narrow temperature range (from 35 to 50 °C). This allowed tracking the dependence in the change of properties of catalysts prepared from various precursors on the reaction temperature, as well as comparing characteristics of the systems under study (Fig. 2).

According to the data obtained, the nature of the palladium precursor does not exert a

significant effect on the degree of acetylene conversion for Pd/Sibunit catalysts. Conversion degrees of $X_{C_2H_2}$ for monometal samples are close in the whole range of the studied temperatures. The selectivity of nonmodified catalysts prepared from $Pd(NO_3)_2$ and $[Pd(NH_3)_4](CH_3COO)_2$ can also be considered comparable.

The introduction of zinc leads to a reliable increase in the degree of acetylene conversion in a given temperature range (35−50 °C) regardless of the precursor selected. At the same time, the Pd−Zn/Sibunit catalyst prepared from nitrates has a larger $X_{C_2H_2}$ than a similar sample obtained from ammonia complexes; an increase in the degree of acetylene conversion is from 10 to 20 abs. %, depending on the reaction temperature. Herewith, a Pd−Zn/Sibunit sample obtained from nitrates exceeds $X_{C_2H_2}$ of monometal Pd catalysts more than twofold.
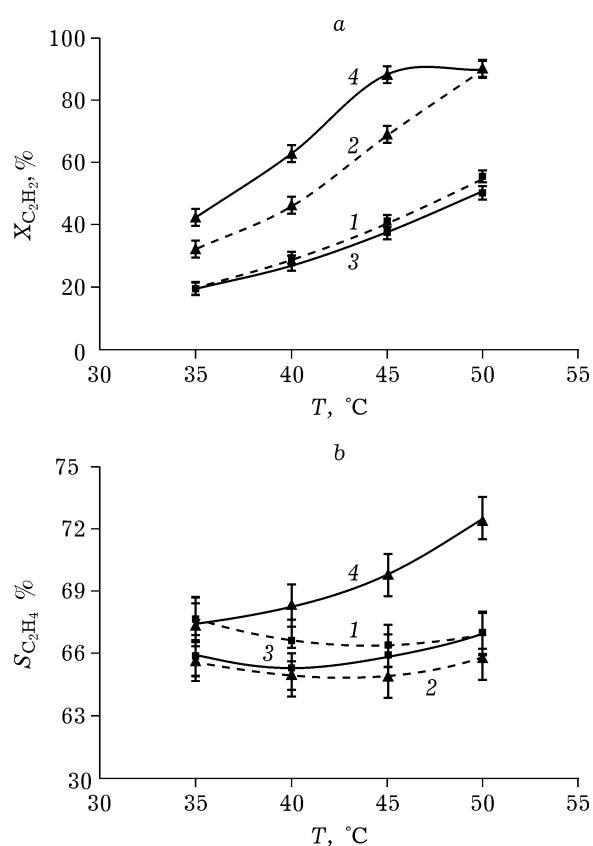

Fig. 2. Acetylene conversion degree (*a*) and selectivity for ethylene (*b*) *vs* reaction temperature for the Pd (*1, 3*) and Pd−Zn (*2, 4*) catalysts prepared from ammonia complexes (*1, 2*) and nitrates (*3, 4*).

The reason for improving characteristics of the activity of zinc modified Pd catalysts can be different dispersity of samples [13]. To verify this suggestion Pd/Sibunit and Pd–Zn/Sibunit catalysts prepared from nitrates and ammoniates were studied by a method for HRTEM. The average diameter of metal particles for Pd/Sibunit and Pd–Zn/Sibunit prepared from nitrates was 4.0 and 1.6 nm, respectively (see Table 1), and for samples prepared from ammoniates – 4.6 and 2.9 nm, respectively. A smaller size of supported particles in bimetal Pd–Zn catalysts is proof that modification of Pd catalyst with zinc prevents the process of its sintering during thermal treatment at 500 °C, regardless of the precursors used. A higher dispersity of the modified samples may explain their greater activity, since the reaction considered is structurally sensitive [2, 15]. According to HRTEM data, catalysts prepared from ammoniates contain larger particles in comparison with similar samples synthesized from nitrates (Fig. 3). Probably sintering of active particles in the reduction process at 500 °C is manifested to a greater extent for samples prepared from ammonia complexes and apparently, a lower temperature is necessary for metal reduction from ammonia solutions, than for reduction of nitrates.

The selectivity of a Pd–Zn catalyst prepared from ammonia complexes is at the level typical for monometal Pd catalysts. At the same time, the preparation of a Pd–Zn sample from $Pd(NO_3)_2$ and $Zn(NO_3)_2$ leads to a significant increase in selectivity for ethylene when carrying out the reaction at $T \geq 40$ °C. One could opine that the reason for the improvement of selectivity on a given catalyst is associated with an increase in the rate of ethylene desorption at elevated temperatures driven by an increase in
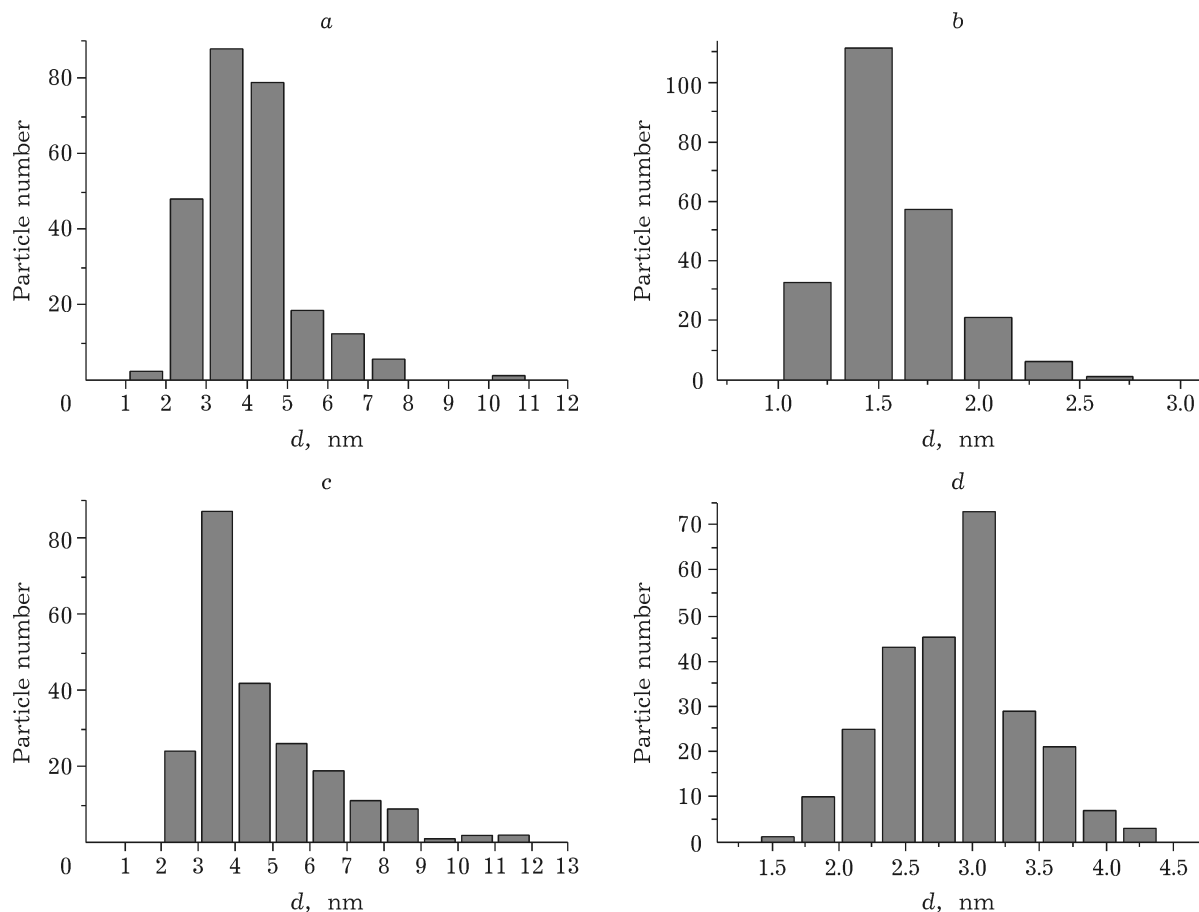

Fig. 3. Histograms of the particle size distribution for various catalysts: a – 0.5 % Pd/Sibunit, b – 0.5 % Pd–0.31 % Zn/Sibunit prepared from nitrates, c – 0.5 % Pd/Sibunit, d – 0.5 % Pd–0.31 % Zn/Sibunit prepared from ammoniates.

the rate of the hydrogenation reaction and the transition of the process to the area, where the catalyst activity is determined by the diffusion rate of components of the reaction mixture to the catalyst grain (see Fig. 2). Additionally, there is a chance that the extent of interactions of palladium with zinc, and consequently, the composition of the resulting bimetal phase and its amount in Pd–Zn samples prepared from different precursors will be different, which also should affect the activity of catalysts and reaction selectivity [12, 16]. Alongside with that, a possible reason for improving $S_{C_2H_4}$ of supported Pd–Zn catalysts synthesized from nitrates is the formation of active canters of a new type. Therefore, to justify this assumption the assessment of kinetic parameters of the hydrogenation process was performed.

Assessment of kinetic characteristics of hydrogenation on Pd/Sibunit and Pd–Zn/Sibunit catalysts

As known from the literature data, the reaction of acetylene hydrogenation to ethylene has the zeroth order by acetylene and the first order by hydrogen [10]. Alongside this, measurements in our case were carried out at intensive shaking of the reactor with the catalyst, which ensured the conditions when the dissolution rate of C_2H_2 and H_2 in the liquid phase was much higher than their conversion rate. The experimental conditions were close to those of perfect mixing. Due to the rapidity of the establishment of equilibrium between the gas and liquid phases (hydrogen solubility in N-methylpyrrolidone is 0.05 cm^3/cm^3 at 20 °C and the atmospheric pressure almost does not depend on the temperature in the studied narrow range [17]), hydrogen concentration is virtually unchanged during the reaction and accordingly, does not affect the process rate.

Assessment of kinetic parameters of hydrogenation that are the apparent activation energy (E_{act}) and pre-exponential factor (ln A) was carried out for Pd/Sibunit and Pd–Zn/Sibunit catalysts synthesized from nitrates and ammoniates. For this purpose, rate dependencies of catalytic hydrogenation of acetylene related to 1 g of catalyst from the reaction temperature in Arrhenius coordinates ($R^2 = 0.999$)
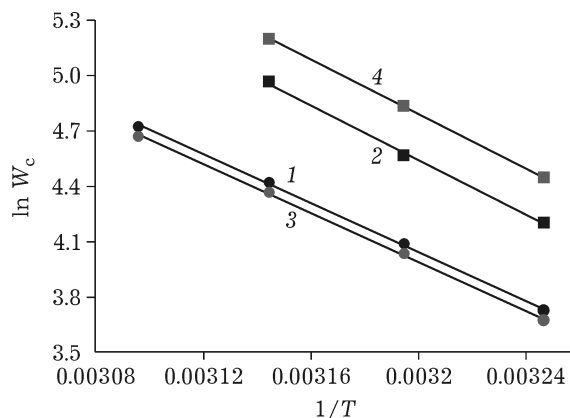

Fig. 4. Acetylene catalytic hydrogenation rate *vs* reaction temperature over Pd (*1*, *3*) and Pd–Zn (*2*, *4*) catalysts prepared from ammonia complexes (*1*, *2*) and nitrates (*3*, *4*).

(Fig. 4) were obtained, and target values of kinetic parameters were determined from the data obtained (Table 2).

As can be seen, calculated values of the E_{act} for all catalysts are found in the range corresponding to the process in the kinetic region [18], in which the reaction rate is determined by the rate of the limiting stage of chemical transformation and its dependence on temperature.

The E_{act} values obtained using samples of identical composition but prepared from different precursors have close values. This testifies that the nature of active centres formed on the surface of catalysts with similar compositions (Pd or Pd–Zn) does not depend on the active component precursor. Much higher values of the activation energy (~7 kJ/mol) than for palladium samples were obtained for zinc-modified samples. Therefore, one can assume that centres where acetylene is sorbed (provided that acetylene activation is the process limiting stage) for catalysts containing zinc will also differ from ac-

TABLE 2

Kinetic characteristics of the acetylene hydrogenation process on modified Pd–Zn/Sibunit and unmodified Pd/Sibunit catalysts

Catalysts	Precursor	E_{act}, kJ/mol	ln A
Pd	Nitrate	54.3	24.9
	Ammoniate	55.1	25.2
Pd–Zn	Nitrate	61.5	28.4
	Ammoniate	62.4	28.6

tive centres formed on unmodified samples, which probably shows of the electron component of modification [19, 20], as well as a part, a consequence of different dispersion (geometrical factor) of mono- and bimetal systems [13, 14].

Alongside this, pre-exponential factor values for catalysts modified with zinc turned out larger in comparison with Pd/Sibunit samples. The results obtained allow assuming that on the modified surface of Pd catalyst, regardless of palladium and zinc precursors used at synthesis, there is a greater number of active centres, on which hydrogenation occurs, which is probably driven by a greater dispersity of Pd–Zn catalysts.

Thus, modification of Pd catalyst with zinc leads to a change in the nature of active centres on the catalyst surface and their number increase. Herewith, catalytic characteristics (E_{act} and ln A) for both Pd/Sibunit and Pd–Zn/Sibunit samples are virtually not dependent on the nature of palladium and zinc precursors.

CONCLUSION

A study conducted demonstrated that the conditions of the synthesis of 0.5 % Pd/Sibunit and 0.5 % Pd–M/Sibunit (M: Ga, Zn, Ag) catalysts (Pd/M = 1 : 1) exerted a significant effect on their properties in the reaction of liquid-phase hydrogenation of acetylene.

The time of reductive thermal treatment to a larger extent affects characteristics of non-modified Pd/Sibunit sample and is manifested in the activity loss at an increase of the time of reduction due to sintering of the active component. On the contrary, modification of Pd catalyst with gallium, zinc, as well as silver stabilizes palladium dispersity by preventing the formation of large particles during thermal treatment (according to HRTEM data), which determines the activity preservation of Pd–M/Sibunit (M: Ga, Zn, Ag) prepared at different times of high temperature exposure.

The precursor nature of the active component does not affect catalytic characteristics of monometal palladium catalysts but reliably affects properties of bimetal Pd–Zn systems. This is manifested in a simultaneous increase in the acetylene conversion degree and selectivity for

ethylene for a Pd–Zn sample prepared from nitrates in comparison with similar catalysts prepared from ammonia metal complexes. But along with that, according to assessment results of kinetic characteristics, modification of the Pd catalyst with zinc leads to a change in the nature of active centres on the catalyst surface and their number increase, regardless of the nature of palladium and zinc precursors. The causes of the difference in catalytic characteristics of Pd–Zn/Sibunit samples prepared from nitrate and ammonia complexes are probably different interaction degrees of palladium and zinc in these systems that is manifested, in particular, in different dispersity of the active component.

REFERENCES

1 Nikolaev S. A., Zanaveskin L. N., Smirnov V. V., Averianov V. A., and Zanaveskin K. L., *Chem. Sust. Dev.*, 78, 3 (2009) 248.
  URL: http://www.sebran.ru/en/jornals/KhUR
2 Borodzicski A., Bond G. C., *Catal. Rev.*, 48, 2 (2006) 91.
3 US Pat. No. 7183451 B2, 2007.
4 US Pat. No. 7692051 B2, 2010.
5 Hou R., Wang T., Lan X., *Ind. & Eng. Chem. Res.*, 52 (2013) 13305.
6 US Pat. No. 0217781 A1, 2011.
7 Mei D., Neurock M., Smith C. M., *J. Catal.*, 268, 2 (2009) 181.
8 Noskov A. S. (Ed.), Promyshlenny Kataliz v Lektsiyakh, issue 2, Kalvis, Moscow, 2006.
9 Krylov O. V., Geterogenny Kataliz, Akademkniga, Moscow, 2004.
10 Shitova N. B., Shlyapin D. A., Afonasenko T. N., Kudria E. N., Tsyrulnikov P. G., Liholobov V. A., *Kinetika i Kataliz*, 52, 2 (2011) 259.
11 Noskov A. S. (Ed.), Promyshlenny Kataliz v Lektsiyakh, issue 1, Kalvis, Moscow, 2005.
12 Mashkovsky I. S., Baeva G. N., Stakheev A. Yu., Vargaftik M. N., Kozitsyna N. Yu., Moiseev I. I., *Mendeleev Commun.*, 24, 6 (2014) 355.
13 Zhao L., Wei Z. Zhu M., Dai B., *J. Ind. Eng. Chem.*, 18, 1 (2012) 45.
14 Komatsu T., Inaba K., Uezono T., Onda A., Yashima T., *Appl. Catal. A: Gen.*, 251 (2003) 315.
15 Yarulin A. E., Krespo-Kecada M. R., Egorova E. V., Kivi-Minsker L. L., *Kinetika i Kataliz*, 53, 2 (2012) 263.
16 Mashkovskiy I. S., Tkachenko O. P., Baeva G. N., Staheev A. Y., *Kinetika i Kataliz*, 50, 5 (2009) 798.
17 Gayle A. A., Zalishchevskiy G. D., N-methylpyrrolidone. Polucheniye, Svoystva i Primeneniye v Kachestve Selektivnogo Rastvoritelya, Khimizdat, St. Petersburg, 2005.
18 Krasnov N. K., Fizicheskaya Khimiya, part 2, Vyssh. shk, 2001.
19 Wang Z., Yang L., Zhang R., Li L., Cheng Z., Zhou Z., *Catal. Today*, 264 (2016) 37.
20 Barrios C. E., Bosco M. V., Baltanas M. A., Bonivardi A. L., *Appl. Catal. B: Environ.*, 179 (2015) 262.