Intermetallic Pd₁–Zn₁ Nanoparticles in the Selective Liquid-Phase Hydrogenation of Substituted Alkynes

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Abstract—A comparative study of the catalytic characteristics of monometallic Pd/α - Al_2O_3 and bimetallic $Pd-Zn/\alpha$ - Al_2O_3 catalysts in the liquid-phase hydrogenation of structurally different substituted alkynes (terminal and internal, symmetrical and asymmetrical) was carried out. It was established that an increase in the reduction temperature from 200 to 400 and 600°C led to a primary decrease in the activity of $Pd-Zn/\alpha$ - Al_2O_3 catalyst containing Pd_1-Zn_1 and agglomeration of Pd_1-Zn_1 intermetallic nanoparticles. The $Pd-Zn/\alpha$ - Al_2O_3 catalyst containing Pd_1-Zn_1 nanoparticles exhibited increased selectivity to the target alkene formation, as compared with that of Pd/α - Al_2O_3 . Furthermore, the use of the $Pd-Zn/\alpha$ - Al_2O_3 catalyst made it possible to more effectively perform the kinetic process control of hydrogenation because the rate of an undesirable complete hydrogenation stage decreased on this catalyst.

Keywords: $Pd-Zn/\alpha-Al_2O_3$, selective liquid-phase hydrogenation, intermetallic compound, selectivity, phenylacetylene, diphenylacetylene, 1-phenyl-1-propyne, 1-phenyl-1-butyne, 4-octyne, terminal alkynes, internal alkynes, styrene

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INTRODUCTION

The catalytic hydrogenation of hydrocarbons containing a triple carbon–carbon bond is a key reaction of contemporary chemistry [1, 2]. Selective hydrogenation is used in large-scale industrial processes for the removal of alkyne compounds (for example, acetylene or phenylacetylene) from commercial olefins to be utilized for the production of polymers [3]. This process is also of paramount importance for fine organic synthesis because the products of selective triple bond hydrogenation—*cis*- and *trans*-olefins—are source materials for the food and pharmaceutical industry; they are also used in a number of processes for the production of detergents, light-emitting diodes, liquid-crystal displays, etc. [4–7].

For the effective reaction performance, hydrogenation catalysts should be highly selective for the target olefin even at the high conversions of a parent alkyne compound [8]. The currently used palladium catalysts are insufficiently selective, and the efforts of researchers are directed toward the development and refinement of methods for improving their catalytic characteristics.

The promotion of Pd catalysts with a second metal is a possible method of increasing selectivity. The bimetallic compositions obtained by alloying possess high selectivity and operational stability under reaction conditions. In the context of the currently available classification, these catalysts containing bimetallic clusters with a specified composition as active components are considered as hybrid systems with adjustable catalytic properties [9, 10]. Among the most commonly used catalysts, Pd–Ag [11, 12], Pd–Au [13], and Pd–Cu [14] should be mentioned.

The Pd–Zn composition is a promising bimetallic system, which finds wide use in hydrogenation reactions. The high selectivity of the Pd–Zn catalysts in the hydrogenation of acetylene into ethylene was found [15-18] and discussed in reviews [19, 20]. Density functional theory (DFT) calculations showed that an increase in the selectivity of the Pd-Zn system is related to a decrease in the heat of adsorption of ethylene because of a change in the Pd electronic structure upon the formation of a bimetallic compound of Pd with Zn [21]. In this case, the activation barrier of ethylene desorption is lower than the activation barrier of its hydrogenation, and olefin desorption from the catalyst surface becomes the preferential reaction path. As a result, the selectivity of the bimetallic catalyst for the formation of ethylene considerably increases in comparison with that of a monometallic analog, although due to a loss of activity.

A unique property of the Pd–Zn composition is the ability to form Pd–Zn intermetallic compounds with a crystal structure different from that of the parent metals. Because of the strict ordering of the intermetallic compound, active centers with a more uniform structure are formed on the catalyst surface; this can facilitate an increase in the catalyst selectivity [22]. For example, Zhou et al. [23] found that the intermetallic Pd–Zn nanosystems possess high selectivity in the hydrogenation of acetylene into ethylene. According to the data of microcalorimetric measurements and DFT calculations, the specific spatial arrangement of Pd sections in the Pd–Zn–Pd ensembles of the intermetallide leads to the moderate σ -binding of acetylene with two adjacent Pd centers and the weak π -binding adsorbed ethylene on individual Pd centers. This facilitates the chemisorption of acetylene and accelerates the desorption of ethylene from the catalyst surface. As a result the selective hydrogenation of acetylene into ethylene becomes kinetically preferable.

Note that the applicability of supported Pd-Zn catalysts to selective liquid-phase hydrogenation reactions of complex organic molecules remains almost unexplored. The characteristics of Pd-Zn catalysts were studied only in the processes of the liquid-phase hydrogenation of phenylacetylene. In this context, note that Yoshida et al. [24] compared the catalytic characteristics of Pd and Pd-Zn samples in the liquidphase hydrogenation of phenylacetylene in a toluene solution. The Pd–Zn catalyst prepared by a coprecipitation method possessed low activity, in comparison with that of a monometallic analog, but higher target selectivity. Furthermore, a decrease in the rate of the second (undesirable) stage of the complete hydrogenation of the target olefin into ethylbenzene on the bimetallic catalyst was found. Wang and coauthors [25] also found increased selectivity in the hydrogenation of phenylacetylene on the supported $Pd-Zn/Al_2O_3$ samples, as compared with the monometallic Pd. The authors showed that a ratio between metal components in the catalyst has an additional effect on selectivity. The sample with Zn/Pd = 6 exhibited maximum selectivity. Unfortunately, Wang et al. [25] did not perform a detailed study of Pd-Zn particles structure and it remains unclear whether the active component occurred on the support surface as the nanoparticles of Pd-Zn alloy with a face-centered cubic (FCC) structure or highly ordered Pd-Zn intermetallic compounds were formed in this case. Furthermore, the properties of Pd–Zn catalysts in the hydrogenation of substituted alkynes with more complex structures were not investigated.

In connection with this, the aim of the present work was to study the characteristics of catalysts based on Pd–Zn nanoparticles in the liquid-phase hydrogenation reactions of structurally different substituted alkynes. A previous study of the Pd–Zn nanoparticles formation on the surface of α -Al₂O₃ showed that the variation of the reductive catalyst activation conditions makes it possible to obtain the supported particles of intermetallic compounds and to almost completely avoid the formation of monometallic Pd clusters [26]. In this case, the reduction temperature exerts a considerable effect on the structure of Pd-Zn nanoparticles. It was found that, on the one hand, particles with an insufficiently ordered structure were formed at relatively low temperatures $(200-400^{\circ}C)$ and an increase in the temperature facilitated the formation of Pd-Zn intermetallic compound nanoparticles. On the other hand, the concentration of Zn on the surface of nanoparticles can decrease at high temperatures because of its evaporation and/or diffusion into the near-surface layers and the bulk of a nanoparticle, which can also negatively affect the catalytic properties. The main goal of this work was to study in detail the catalytic characteristics of Pd–Zn/ α -Al₂O₃ samples, which were activated at different temperatures, in the liquid-phase hydrogenation of structurally different terminal and internal alkynes.

EXPERIMENTAL

Catalyst Preparation

The 3 wt % Pd–1.8 wt % Zn/ α -Al₂O₃ bimetallic catalysts were prepared by the incipient wetness impregnation of a preliminarily calcined (550°C, air) support (α -Al₂O₃, $S_{sp} = 8 \text{ m}^2/\text{g}$, Alfa Aesar) with the aqueous solutions of the nitrates Pd(NO₃)₂ and $Zn(NO_3)_2$. Metal concentrations in the solution were calculated in such a way as to obtain a molar ratio of 1:1 between the metals in the catalyst. For studying the temperature dependence of the intermetallic nanoparticles formation, a series of Pd-Zn samples reduced at 200, 400, 600, and 800°C (in 5% H₂/Ar for 2 h) was synthesized. After drving, the samples were immediately reduced without preliminary heat treatment. The reference monometallic 1 wt % Pd/ α -Al₂O₃ catalyst was also obtained by incipient wetness impregnation with an aqueous solution of the nitrate $Pd(NO_3)_2$. A series of the samples reduced at 200, 400, 600, and 800°C was prepared.

Liquid-Phase Hydrogenation

The liquid-phase hydrogenation of phenylacetylene (98%, Aldrich) and other substrates (styrene, diphenylacetylene, 1-phenyl-1- propyne, 1-phenyl-1butyne, and 4-octyne; all of the substrates with 99% purity were purchased from Aldrich) were carried out in an autoclave type reactor with a magnetic stirrer and a gas supply system. The autoclave was equipped with a sampling system and an electronic pressure gage for the monitoring of the degree of hydrogen absorption. The reaction was performed in *n*-hexane (98%, Merck) at 25°C and an initial hydrogen pressure of 10 bar. The catalyst sample weight and the intensity of stirring were chosen to perform the process in the kinetic region. The procedure used for the determination of process conditions was described in detail earlier [27].

The reaction mixture was analyzed by chromatography on a Kristall 5000 instrument (Khromatek,



Fig. 1. General view of a kinetic curve of the dependence of the amount of absorbed hydrogen A_{H_2} on the reaction time of the liquid-phase hydrogenation of phenylacetylene (PA).

Russia) with a flame-ionization detector. The reaction mixture was analyzed on an HP5-MS column (5% phenyl dimethylsiloxane; 30 m; inner diameter, 0.25 mm; stationary phase film thickness, 0.25 µm; and carrier gas, helium). It was found that aromatic ring hydrogenation did not occur under the reaction conditions. Furthermore, it was established that, on the hydrogenation of phenylacetylene in a hydrogen absorption range of 0.1-0.5 equiv H₂ (the first stage of hydrogenation), the amount of ethylbenzene formed was no higher than 0.2 mol % on a total basis (phenylacetylene + styrene + ethylbenzene), and the occurrence of complete hydrogenation reaction can be ignored. The analysis of the reaction mixture at the second stage of reaction (in a hydrogen absorption range of 1.2-1.5 equiv H₂) showed that the residual phenylacetylene amount was no higher than 0.5% and the absorption of hydrogen during hydrogenation was also negligibly small. A similar result was also obtained for the other substrates.

The reaction rate $r \pmod{1}_{H_2} \operatorname{mg}_{Cat}^{-1} \operatorname{min}^{-1}$ was determined based on the rate of hydrogen absorption from a graph of the dependence of the amount of absorbed hydrogen on the reaction time (Fig. 1). Because the hydrogenation reaction of alkyne compounds occurs in two stages, the reaction rate was determined for each of them: in an absorption range of 0.1-0.5 equiv H₂ for the first stage (r_1) or 1.2-1.5 equiv H₂ for the second stage (r_2).

The catalytic activity of the test samples at each stage of the reaction was evaluated from the turnover frequency (TOF, s^{-1}). Taking into account the fact that, in the case of bimetallic catalysts, the amount of surface Pd atoms cannot be determined by electron microscopy because a part of the surface is occupied

by the atoms of the second metal, the value of TOF was calculated based on the total number of palladium atoms (N_{Pd}) in the catalyst via the formula

$$\Gamma OF = \frac{r}{N_{\rm Pd}}.$$
 (1)

Selectivity in the formation of target olefin ($S_{=}$) was determined based on the data of the chromatographic analysis of the reaction mixture according to Eq. (2), where $n_{=}$ and n_{-} are the mole fractions of the resulting olefin and alkane, respectively:

$$S_{=} = \frac{n_{=}}{n_{=} + n_{-}}.$$
 (2)

The effectiveness of the kinetic process control was evaluated by comparing the r_1/r_2 ratios between the rates of parent alkyne hydrogenation at the first and second stages [28, 29].

RESULTS AND DISCUSSION

Phenylacetylene Hydrogenation

Comparison between the activities of Pd and Pd–Zn catalysts. The hydrogenation of phenylacetylene was studied in detail [24, 25, 30, 31]. The reaction occurs via a classical two-stage mechanism. At the first stage, the predominant hydrogenation of parent phenylacetylene to styrene occurs, and it is accompanied by the absorption of 1 equiv H₂. At the second stage, the resulting styrene is hydrogenated to ethylbenzene; in this case, the second equivalent of H₂ is absorbed. Figure 2 shows the characteristic kinetic curves of the time dependence of the amount of absorbed hydrogen for reactions performed on Pd/ α -Al₂O₃ and Pd–Zn/ α -Al₂O₃ reduced at different temperatures.

An analysis of the initial section of kinetic curves for both mono- and bimetallic catalysts showed that the reaction rate was almost independent of the degree of conversion of initial phenylacetylene, and they were linear up to the absorption of 0.8-0.9 equiv H₂ (Fig. 2). The linear dependence indicates that the rate of a triple bond hydrogenation has a zero order with respect to phenylacetylene, which is consistent with published data. Thus, it was found [27, 32, 33] that, on the hydrogenation of an alkyne compound, the zero order with respect to a reactant was retained up to the high degrees of conversion because of its strong adsorption. The results of the comparative calculations of the heats of adsorption of alkyne and alkene compounds (based on an example of acetylene) [34–36] indicated that the heat of adsorption of an alkyne (1.6 eV) is much higher than that of an alkene (1.0 eV). As a result, high surface coverage was retained even at small concentrations of the initial alkyne.

The activities of the Pd/α - Al_2O_3 and $Pd-Zn/\alpha$ - Al_2O_3 catalysts were compared based on the values of



Fig. 2. Dependence of the amount of absorbed hydrogen A_{H_2} on the reaction time of the liquid-phase hydrogenation of phenylacetylene (PA) on (\bullet) the monometallic 1% Pd/ α -Al₂O₃ (800°C) catalyst and the bimetallic 3% Pd-1.8% Zn/ α -Al₂O₃ catalyst reduced at different temperatures: (\triangle)200, (\Box) 400, (\bigcirc) 600, and (\times)800°C.

 TOF_1 calculated from the rates of phenylacetylene hydrogenation at the first stage of the process (Table 1). A comparison between the values of TOF_1 for monometallic and bimetallic Pd-Zn catalysts reduced at identical temperatures (Table 1) showed that the activity of the Pd–Zn/ α -Al₂O₃ samples was lower by a factor of 3-9 than that of monometallic ones. Note that analogous data were obtained previously by Wang et al. [25]. A decrease in the catalytic activity of the samples based on supported Pd–Zn nanoparticles in the hydrogenation of phenylacetylene was found and explained by the influence of geometric effects. On the surface of bimetallic particles, palladium atoms predominantly occurred in the environment of zinc atoms, which do not exhibit catalytic activity in this reaction. As a result, the number of the Pd active centers at which hydrogenation occurs decreased to cause a decrease in the total activity. An analogous effect of a decrease in the activity was also observed on Pd-Cu [27], Pd-In [37, 38], and Pd–Ag [39] bimetallic catalysts, in which the second metal did not possess essential activity in the reaction of hydrogenation, and discussed by Schlögl with coworkers [40, 41] as applied to the Pd-Ga systems.

Effect of reduction temperature on the activity of Pd and Pd–Zn catalysts. Because it was established earlier that the structure of metallic Pd–Zn nanoparticles to a considerable degree depends on the catalyst reduction temperature, it is of interest to analyze the influence of this factor on the catalytic characteristics. Figure 3 shows the dependence of the reaction rate on the catalyst reduction temperature for the Pd/α - Al_2O_3 and $Pd-Zn/\alpha$ - Al_2O_3 catalysts. The monometallic samples exhibited a gradual decrease in the value of TOF₁ by a factor of about 1.8 as the reduction temperature was increased. According to electron-microscopic data, this was related to the agglomeration of Pd^0 nanoparticles and an increase in their size from 5– 7 nm for the sample reduced at 200°C to 30–40 nm for Pd/α - Al_2O_3 reduced at 800°C; this led to a decrease in the surface area accessible to the reaction [26].

For the $Pd-Zn/\alpha$ - Al_2O_3 catalyst, an increase in the reduction temperature from 200 to 400°C led to a sharp decrease in the reaction rate, which decreased by

a factor of >2 from 70 to 34 mmol_{H₂} min⁻¹ mg_{Cat}⁻¹. This considerable decrease in the activity of the bimetallic catalyst, as compared with the monometallic Pd/ α -Al₂O₃, can be explained by the following two factors: (1) the agglomeration of metal nanoparticles and (2) the disappearance of monometallic Pd nanoparticles with the subsequent formation of Pd–Zn intermetallide nanoparticles [26]. As the reduction temperature was further increased to 600°C, the rate of hydrogenation continued to decrease, although not so sharply. This can occur because of both the continuous agglomeration of a metal phase and the formation of Pd–Zn intermetallic compound nanoparticles with a more ordered structure.

An unexpected result was obtained for $Pd-Zn/\alpha$ - Al_2O_3 reduced at 800°C. It was found that an increase in the temperature from 600 to 800°C led to a more

Reduction temperature	Catalyst	$r_1 \times 10^{3*}$	TOF ₁ **	TOF ₂ **	TOF ₁ /TOF ₂	
200°C	Pd	67.4	2.4	1.1	2.2	
	Pd-Zn	69.4	0.8	0.06	13.6	
400°C	Pd	60.2	2.1	0.9	2.3	
	Pd-Zn	33.6	0.4	0.04	10.6	
600°C	Pd	59.0	2.1	1.1	1.9	
	Pd-Zn	20.9	0.3	0.02	10.7	
800°C	Pd	37.6	1.3	0.62	2.2	
	Pd-Zn	44.6	0.5	0.05	11.7	

Table 1. Kinetic characteristics of the liquid-phase phenylacetylene hydrogenation in the presence of monometallic $1\% Pd/\alpha$ -Al₂O₃ and bimetallic $3\% Pd-1.8\% Zn/\alpha$ -Al₂O₃ reduced at different temperatures

* $mol_{H_2} min^{-1} g_{Cat}^{-1}$.

** s⁻¹

than twofold increase in the catalytic activity, as compared with the sample reduced at 600°C: r_1 increased from 21 to 45 mol_{H₂} min⁻¹ g_{Cat}^{-1} in spite of an increase of the Pd–Zn nanoparticles size. The most probable explanation for this fact consists in the zinc deficiency of the surface of bimetallic particles. According to the study of the surface composition by XPS, the surface concentration of Zn decreased by a factor of 4 as the reduction temperature was increased from 400 to 800°C [26].

The decrease of the Zn surface concentration at a high temperature can be caused by both its diffusion into the bulk of bimetallic nanoparticles and evaporation from the surface of nanoparticles. Holzapfel et al. [42] demonstrated the possibility of Zn diffusion. Based on the data obtained by TPD and IR-CO methods, they made a conclusion on alloy decomposition in the course of high-temperature treatment, which led to an



Fig. 3. Dependence of the reaction rate of the liquid-phase hydrogenation of phenylacetylene on the catalyst reduction temperature for Pd/α -Al₂O₃ and Pd-Zn/ α -Al₂O₃.

increase in the surface fraction occupied by palladium atoms. Thus, a peak at ~1947 cm⁻¹, which corresponds to CO adsorbed in a bridging form, was detected in the IR-CO spectra of the Pd–Zn sample reduced at 400°C; this is indicative of the appearance of multiatomic Pd_n centers in the structure of the catalyst. As the reduction temperature was increased to 650°C, the peak intensity of CO adsorbed in a bridging form increased. In this case, a shift of the linearly adsorbed CO peak from 2075 to 2087 cm⁻¹, which is characteristic of CO adsorption on Pd(III), was observed.

The desorption of zinc from the surface at high temperatures can be an alternative mechanism of decreasing the surface concentration of zinc. With the use of a set of physicochemical techniques, it was found [20, 43] that the destruction of the Pd–Zn alloy occurred as a result of Zn evaporation at a temperature higher than 600°C. Thus, the observed increase in the activity of Pd–Zn/ α -Al₂O₃ after its high-temperature reduction at 800°C may be related to an analogous change in the surface structure of nanoparticles.

Comparison of the ratios between the rates of hydrogenation at the first and second stages on the Pd and Pd–Zn catalysts. The TOF_1/TOF_2 ratio between the rates of hydrogenation at the first and second stages of the process is an important kinetic parameter, which characterizes the selective hydrogenation reactions of alkyne compounds. A decrease in the rate of reaction at the second stage makes it possible to more effectively control the process kinetics and to stop the reaction at the necessary point in time for preventing the excessive hydrogenation of an olefin intermediate. Therefore, the TOF_1/TOF_2 ratio is an important characteristic of a catalyst, which should be taken into consideration in the analysis of its catalytic properties [28].

According to the data of a kinetic study (Fig. 2), on going from the first to the second stage of hydrogenation on monometallic Pd/α -Al₂O₃ (after the absorption of 1 equiv H₂), the rate of reaction decreased insignifi-

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cantly; this is evident from the smooth kinetic curve, which does not have clearly pronounced bends in this region. The calculation of the ratio between the rates of hydrogenation for the monometallic Pd/ α -Al₂O₃ catalysts, which is given in Table 1, shows that the average value of this parameter is ~2.1 ± 0.1.

The kinetic curves for the Pd–Zn catalysts had another shape. All of the bimetallic catalysts exhibited a clearly pronounced bend after the absorption of ~1 equiv H₂, which is indicative of considerable reaction retardation on going from the first to the second stage. The TOF₁/TOF₂ ratio for the Pd–Zn/ α -Al₂O₃ catalysts was 11.8 ± 0.9; that is, the decrease of the hydrogenation rate upon going from the first to the second stage of the process was pronounced to a considerably larger degree than that for the monometallic Pd/ α -Al₂O₃ sample (Fig. 2).

An analysis of the literature showed that the predominant decrease in the rate of hydrogenation at the second stage of the reaction and, as a consequence, the appearance of a characteristic bend in the kinetic curves of hydrogen absorption for the Pd–Zn/ α -Al₂O₃ catalysts can be explained by two factors:

(1) The suppression of the formation of a PdH_r phase as a result of the formation of bimetallic Pd-Zn particles. It is widely known that, under normal conditions, palladium metal can dissolve a considerable amount of hydrogen to form α - and β -PdH_x hydride phases [1, 44, 45]. In the course of reaction, the hydrogen constituent of a hydride migrates to the surface of palladium and facilitates the complete hydrogenation of an olefin intermediate adsorbed on the surface by reacting with it [24, 46]. The use of bimetallic alloy catalysts makes it possible to avoid the formation of a hydride phase or to substantially decrease its quantity. A similar effect was observed in bimetallic systems such as Pd–Ge, Pd–Sb, Pd–Sn, Pd–Pb [47], Pd-Ga [39, 48, 49], Pd-Ag [50], and Pd-Zn [19]. The suppression of Pd hydride formation as a result of the formation of bimetallic Pd-In nanoparticles was also found by the temperature programmed desorption of hydrogen in the Pd–In systems [37].

(2) Another possible factor is a change in the electronic structure of Pd as a result of the formation of an alloy or Pd–Zn intermetallic compound. Thus, Wang et al. [25] studied the electronic structure of Pd–Zn nanoparticles supported onto Al₂O₃ by XPS and found that the Pd3*d*_{5/2} peak in the spectra of Pd–Zn/Al₂O₃ was shifted toward higher binding energies by ~0.4–0.5 eV, as compared with that of Pd/Al₂O₃. The observed increase in the binding energy of the Pd3*d*_{5/2} peak indicates an electron density shift from the atoms of Pd to the atoms of Zn [51–53]. An analogous effect was observed in a study of the Pd/ZnO catalyst [24]. With the use of XPS, it was established that, upon the formation of Pd–Zn alloy, the Pd3*d*_{5/2} line shifted from 355.2 to 355.8 eV. A similar result was obtained in

 Zn_1 NANOPARTICLES 485 a comprehensive study of the structure of Pd– Zn/α -

Al₂O₃ synthesized for this work [26]. For the reduced catalysts, the binding energy of the Pd3 $d_{5/2}$ peak was ~335.6 eV, and it was shifted by 0.5 eV relative to Pd⁰ standard; this fact is indicative of a decrease in electron density on the atoms of Pd and an increase in their electron deficiency. The above allowed us to assume that the decrease of electron density on the atoms of Pd facilitates the desorption of styrene from the catalyst surface into the solution and decreases the rate of its hydrogenation [19, 24, 51].

Thus, based on an analysis of the experimental results and published data, we can conclude that, upon the formation of intermetallic Pd–Zn nanoparticles, the observed decrease in the hydrogenation rate at the second stage of the process is caused by the predominant decrease in the activity of the Pd–Zn/ α -Al₂O₃ bimetallic catalyst in the hydrogenation of an olefin, as compared with activity in the hydrogenation of the parent alkyne.

To confirm this hypothesis, we carried out a comparative study of the hydrogenation rate of styrene and phenylacetylene on the Pd–Zn bimetallic and Pd monometallic catalysts. The rates of hydrogenation were determined based on the hydrogen absorption rates at low degrees of the initial substrates conversion (see Experimental). The ratio between the rates of hydrogenation of phenylacetylene and styrene ($r_{styrene}/r_{phenylacetylene}$) measured in two independent experiments was used as a criterion for evaluating the effect of zinc on the rate of styrene hydrogenation. The commercial Lindlar catalyst (5%Pd–4%PbO/CaCO₃, Aldrich-62145) was studied as a reference catalyst.

The results of the comparative measurement of the hydrogenation rates (Table 2) show that the ratio between the hydrogenation rates of phenylacetylene and styrene $(r_{\text{styrene}}/r_{\text{phenylacetylene}})$ on monometallic Pd nanoparticles was 3.27, which is consistent with published data, according to which an alkene is hydrogenated more rapidly than a corresponding alkyne [1]. If hydrogenation was carried out on the Pd–Zn/ α -Al₂O₃ sample, the value of $r_{\rm styrene}/r_{\rm phenylacetylene}$ decreased to \sim 2.0; that is, the relative rate of styrene hydrogenation decreased by a factor of 1.6. Analogous data were obtained by Wowsnick et al. [54] for the Pd-Ga catalyst. It is possible to conclude that, although the formation of a Pd–Zn intermetallic compound decreases the total catalyst activity, the activity decreased to a greater degree at the styrene hydrogenation stage; this makes it possible to more effectively implement the kinetic control of the process performed on the Pd–Zn catalyst.

Selectivity of catalysts in the formation of a target olefin. The dependence of selectivity to styrene formation on the conversion of initial phenylacetylene was studied for the Pd–Zn/ α -Al₂O₃ catalysts reduced at 200, 400, 600, and 800°C. The commercial Lindlar catalyst was used as a reference sample (Fig. 4).

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Catalyst	Substrate	$r_{\rm hydr} \times 10^{3**}$	$r_{\rm styrene}/r_{\rm phenylacetylene}$	TOF ₁ ***	TOF ₂ ***
Pd	Phenylacetylene	37.6	3.2	1.3	0.62
	Styrene	123.0	5.2	—	4.4
Pd–Zn	Phenylacetylene	44.6	2.0	0.5	0.05
	Styrene	90.4	2.0	—	1.1
Lindlar	Phenylacetylene	27.6	0.4	0.4	0.03
	Styrene	11.9	0.4	_	0.17

Table 2. Kinetic characteristics of the liquid-phase reactions of phenylacetylene and styrene hydrogenation in the presence of the monometallic 1% Pd/ α -Al₂O₃* and bimetallic 3% Pd-1.8% Zn/ α -Al₂O₃* catalysts and the Lindlar catalyst

A dash denotes that the stage of phenylacetylene hydrogenation was absent with the use of styrene. * The catalysts were reduced at 800°C.

** $mol_{H_2} min^{-1} g_{Cat}^{-1}$.

 $*** s^{-1}$.

At conversions of no higher than 50%, all catalysts demonstrate the target selectivity around 93–96%. In the region of high phenylacetylene conversions, this characteristic gradually decreased for all of the samples. As the conversion of phenylacetylene increased to \geq 90%, selectivity decreased to 80–85%.

According to the classical two-stage mechanism of hydrogenation adapted to liquid-phase processes [55, 56], the experimental data can be explained as follows: In the region of low phenylacetylene conversions, the main reason for a decrease in selectivity is the direct hydrogenation of an adsorbed olefin intermediate (a kinetic factor). This is due to the fact that the concentration of formed styrene in the solution is small and the process of its readsorption can be neglected. In this case, the observed high selectivity indicates that the



Fig. 4. Dependence of the selectivity of styrene formation (S_{styrene}) on the conversion of phenylacetylene in the liquid-phase phenylacetylene hydrogenation on the monometallic Pd/ α -Al₂O₃ (800°C) and bimetallic Pd–Zn/ α -Al₂O₃ catalysts reduced at different temperatures and on the Lindlar catalyst.

contribution of the direct hydrogenation reaction of the adsorbed olefin intermediate to the course of the reaction is small and the second stage of hydrogenation predominantly proceeds through the readsorption of the resulting olefin [55].

With increasing the conversion of phenylacetylene, the concentration of styrene in the reaction solution increased; as styrene accumulated, it began to displace the initial alkyne from the catalyst surface because of the alkyne/alkene competitive adsorption (a thermodynamic factor). As a result of an increase of readsorbed styrene amount on the catalyst surface, the rate of its hydrogenation increased to cause the formation of ethylbenzene and a decrease in the selectivity.

The comparison of the catalytic properties of the $Pd-Zn/\alpha-Al_2O_3$ samples reduced at temperatures of 200, 400, 600, and 800°C showed that the catalyst reduced at 200°C exhibited the lowest selectivity in the phenylacetylene hydrogenation over the entire range of conversions. At a ~90% conversion of phenylacetylene, the value of $S_{=}$ was no higher than 85–86%. The catalysts reduced at 400–800°C were noticeably more selective ($S_{=} ~ 91-93\%$) at the same values of phenylacetylene conversion. It should also be noted that the values of $S_{=}$ for these samples were the same as those for the commercial Lindlar catalyst (Fig. 4).

The low selectivity of the sample reduced at 200°C can be explained by the fact that this temperature is insufficient for the completion of the Pd–Zn intermetallide nanoparticles formation. According to the XRD analysis data, after the reduction of Pd–Zn/ α -Al₂O₃ at 200°C, the XRD pattern of the catalyst exhibited a number of diffraction peaks that indicated the formation of both a solid solution of Pd with Zn and a Pd–Zn intermetallic compound. At the same time, a Bragg peak at 20 ~41.5°, which is characteristic of a palladium metal phase [26], was retained in the XRD pattern. An increase in the reduction temperature to 400–800°C led to the transformation of Pd-containing nanoparticles into the Pd–Zn intermetallic nanopar-

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Substrate	Catalyst	$r_1 \times 10^{3*}$	$r_2 \times 10^{3*}$	TOF ₁ **	TOF ₂ **	r_1/r_2
	Pd	53.0	3.12	1.88	0.11	17.01
	Pd–Zn	13.9	0.43	0.16	0.005	32.69
	Pd	80.7	0.98	5.72	0.07	82.56
$H_3C \longrightarrow CH_3$	Pd-Zn	93.0	0.82	2.20	0.02	113.87
	Pd	18.3	3.68	0.65	0.13	4.98
CH3	Pd-Zn	38.8	1.35	0.46	0.02	28.70
	Pd	3.1	0.85	0.11	0.03	3.68
СН 3	Pd–Zn	1.8	0.14	0.02	0.002	12.19

Table 3. Kinetic characteristics of the liquid-phase reactions of hydrogenation of different substrates in the presence of the monometallic 1% Pd/ α -Al₂O₃ and bimetallic 3% Pd–1.8% Zn/ α -Al₂O₃ catalysts reduced at 600°C

 $mol_{H_2} min^{-1} g_{Cat}^{-1}$.

ticles, which facilitated an increase in the selectivity of the catalyst. Chin et al. [57] obtained an analogous result. They found that the Pd/ZnO catalyst reduced at 350°C was more selective than the sample activated at 125°C; this fact can be explained by the presence of a large amount of palladium metal in the structure of the latter.

It is likely that a relatively rapid decrease in selectivity in the region of high phenylacetylene conversions on both the Pd-Zn catalysts and the Lindlar catalyst was related to the special features of the triple bond geometry in the molecules of terminal alkynes. In a number of publications [27, 58, 59] it was shown that terminal alkynes possess higher reactivity than that of internal alkynes. This can lead to the complete hydrogenation of an intermediate olefin to an alkane even on the Lindlar catalyst [58]. A similar result was also obtained earlier in the hydrogenation of phenylacetylene on the samples containing supported Pd–In particles [38].

Symmetric Alkyne Hydrogenation

The Pd and Pd-Zn catalysts reduced at 600°C were chosen for studying the catalytic properties in the hydrogenation of different substrates.

A comparison of the kinetic curves of hydrogen absorption in the course of the hydrogenation reactions of diphenylacetylene (DPA) and 4-octyne on the Pd/α -Al₂O₃ and $Pd-Zn/\alpha$ -Al₂O₃ catalysts and the values of TOF_1 calculated on their basis (see Figs. 5a, 5c and Table 3) allowed us to conclude that the monometallic Pd catalyst is substantially more active than Pd–Zn/ α -Al₂O₃. In the hydrogenation of diphenylacetylene, the value of TOF₁ calculated for Pd/ α -Al₂O₃ was higher by a factor of 11 than this value for $Pd-Zn/\alpha-Al_2O_3$. In the hydrogenation of 4-octyne,

the value of TOF₁ for Pd/ α -Al₂O₃ was higher by a factor of 2.5 than that for the bimetallic sample. The experimental data are consistent with the results of phenylacetylene hydrogenation (see the previous section), and they are also indicative of the Pd–Zn/ α -Al₂O₃ catalyst lower activity, as compared with that of the monometallic samples.

An analysis of the shapes of the kinetic curves of diphenylacetylene and 4-octyne hydrogenation on both the mono- and bimetallic catalysts showed that for both substrates, a sharp bend was observed after the absorption of 1 equiv H_2 , which indicated a decrease in the rate of hydrogenation on going from the first to the second stage (Figs. 5a, 5c). Note that the effect of the preferred retardation of the second stage of reaction for diphenylacetylene and 4-octyne was pronounced to a considerably larger degree than that for other substrates: it will suffice to compare data in Fig. 5 with the kinetic curves obtained on the hydrogenation of phenylacetylene (Fig. 2), 1-phenyl-1-butyne, and 1-phenyl-1-propyne (Figs. 6a, 6c).

It is likely that the appearance of a bend is related to the geometry of a substrate molecule and the specific character of its adsorption on the catalyst surface. For example, on the hydrogenation of phenylacetylene and other asymmetrical alkynes (see below), a bend in the kinetic curve is pronounced to a much smaller degree than that for diphenylacetylene and 4-octynecompounds with symmetrical structures. A similar result was obtained by Spee et al. [28], who observed a considerably larger retardation of the second stage of the process in the hydrogenation of internal alkynes with symmetrical structures.

A comparative analysis of the shapes of kinetic curves for Pd/ α -Al₂O₃ and Pd–Zn/ α -Al₂O₃ made it possible to conclude that the effect of the preferred decrease of the second reaction stage rate was pro-



Fig. 5. Dependences of the amount of absorbed hydrogen A_{H_2} on the reaction time (a, c) and of selectivity to olefin formation on alkyne conversion (b, d) in the hydrogenation of (a, b) diphenylacetylene (DPA) and (c, d) 4-octyne on the Pd/ α -Al₂O₃ and Pd–Zn/ α -Al₂O₃ catalysts reduced at 600°C.

nounced to a much larger degree for $Pd-Zn/\alpha$ - Al_2O_3 than for Pd/α - Al_2O_3 . This was confirmed by the data of the quantitative analysis of the rates: the ratios of the rates of the first and second stages of diphenylacetylene hydrogenation (TOF₁/TOF₂) were ~17 and ~33 for the Pd and Pd-Zn catalysts, respectively (see Table 3). In the hydrogenation of 4-octyne, the TOF₁/TOF₂ ratios were 83 and 114 for the Pd and Pd-Zn samples, respectively.

An analysis of "Selectivity to alkene formation– DPA conversion" plot (Fig. 5b) showed that the selectivity of the samples approached 100% in the region of low diphenylacetylene conversions. However, at high conversions, this characteristic was noticeably higher for the Pd–Zn catalyst than for Pd/ α -Al₂O₃. This experimental result is consistent with data on the hydrogenation of phenylacetylene, which are also indicative of an increase in the reaction selectivity upon the formation of intermetallic Pd–Zn particles, as confirmed by [19]. In the case of 4-octyne, the influence of Pd–Zn intermetallic compound formation on the process selectivity was expressed to a lesser degree, and the selectivity of the Pd and Pd–Zn catalysts was almost identical in the entire range of conversions (Fig. 5d).

Asymmetric Alkyne Hydrogenation

Figures 6a and 6c show the dependence of the hydrogen absorption on the reaction time in the hydrogenation of asymmetric alkynes (1-phenyl-1-butyne and 1-phenyl-1-propyne) on the Pd and Pd–Zn catalysts. The formation of Pd–Zn intermetallic compounds leads to an insignificant decrease in the catalytic activity, as compared with that of monometallic Pd. The values of TOF₁ obtained in the hydrogenation of 1-phenyl-1-butyne on the Pd and Pd–Zn samples

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Fig. 6. Dependences of the amount of absorbed hydrogen A_{H_2} on the reaction time (a, c) and of selectivity for olefin formation on alkyne conversion (b, d) in the hydrogenation of (a, b) 1-phenyl-1-butyne and (c, d) 1-phenyl-1-propyne on the Pd/ α -Al₂O₃ and Pd–Zn/ α -Al₂O₃ catalysts reduced at 600°C.

were 0.65 and 0.46 s⁻¹, respectively (Table 3). The bimetallic Pd–Zn catalyst was also less active than the monometallic one in the hydrogenation of 1-phenyl-1-propyne. The value of TOF_1 (0.02) for this catalyst was lower than that for Pd (0.11) by a factor of 5.

In contrast to the hydrogenation of symmetrical compounds, a bend in the kinetic curves for asymmetrical substrates in the region of an equimolar H_2 quantity absorption was not so clearly pronounced, although a tendency toward reaction retardation on going to the second stage was also observed (Table 3, Figs. 6a, 6c). As in the hydrogenation reactions of other substrates, the rate ratio TOF₁/TOF₂ increased on going from Pd/ α -Al₂O₃ to Pd–Zn/ α -Al₂O₃. Thus, in the hydrogenation of 1-phenyl-1-butyne, the value of TOF₁/TOF₂ for Pd–Zn/ α -Al₂O₃ was higher than this ratio for monometallic Pd/ α -Al₂O₃ by a factor of

more than 5. In the hydrogenation of 1-phenyl-1-propyne, the value of TOF_1/TOF_2 for Pd–Zn/ α -Al₂O₃ was also higher by a factor of 3 than that for Pd/ α -Al₂O₃.

An analysis of the dependence of the selectivity of the Pd/α - Al_2O_3 and $Pd-Zn/\alpha$ - Al_2O_3 catalysts in the formation of alkene compounds on the conversion of initial alkynes showed that the catalyst containing Pd-Zn intermetallide nanoparticles as an active component exhibited much higher selectivity than that of monometallic Pd/α - Al_2O_3 in the hydrogenation of both 1-phenyl-1-butyne (Fig. 6c) and 1-phenyl-1-propyne (Fig. 6d). These results are consistent with data obtained in the hydrogenation of the other substrates: phenylacetylene, diphenylacetylene, and 4-octyne.

Note that the high values of $S_{=}$ were obtained on the hydrogenation of asymmetrical alkynes on Pd– Zn/ α -Al₂O₃ in the entire range of the initial alkyne conversions. This is related to the fact that on the hydrogenation asymmetrical alkynes noticeable amounts of complete hydrogenation products were formed already at the very beginning of the process at a low conversion. The observed regularity indicates that the contribution of the direct hydrogenation of adsorbed olefin intermediates on the hydrogenation of asymmetrical alkynes plays a noticeably greater role than that in the hydrogenation of structurally symmetrical molecules.

CONCLUSIONS

In general, the results of a comparative study of the characteristics of the monometallic 1%Pd/ α -Al₂O₂ and bimetallic Pd–Zn/ α -Al₂O₃ catalysts in the selective liquid-phase hydrogenation of structurally different alkynes allowed us to draw the following basic conclusions: We established that the catalytic activity of the bimetallic catalyst in acetylene bond hydrogenation was lower by a factor of 3-10 than the activity of its monometallic analog in the hydrogenation of all of the substrates. As the catalyst reduction temperature was increased from 200 to 600°C, difference in the activities increased. According to the data of an earlier physicochemical study, this is related to the formation and agglomeration of Pd_1-Zn_1 intermetallic nanoparticles in the Pd–Zn/ α -Al₂O₃ catalyst and the disappearance of monometallic Pd ones. The favorable process kinetics is an advantage of the catalyst containing Pd–Zn intermetallide nanoparticles as active sites. Thus, for all of the substrates investigated in this work, the rate of hydrogenation of an initial acetylene compound on Pd–Zn/ α -Al₂O₃ was higher than the rate of the undesirable hydrogenation of the target alkene by a factor of 10–100. This fact makes it possible to perform the effective kinetic control of the process and to stop the reaction upon the completion of the first stage. The Pd– Zn/α -Al₂O₃ catalyst possesses higher selectivity than that of its monometallic analog. A detailed analysis of the kinetic characteristics obtained and the available published data makes it possible to conclude that different catalytic properties of Pd–Zn/ α -Al₂O₃ and Pd/ α -Al₂O₃ are related to the lower adsorption energies of the initial alkyne and an olefin intermediate, which is formed upon its hydrogenation, on the Pd_1 – Zn_1 intermetallic nanoparticles. On the one side, this leads to a decrease in the hydrogenation rate on the Pd–Zn/ α -Al₂O₃ catalyst, as compared with that on Pd/ α -Al₂O₃. However, on the other hand, the lowered adsorption energy facilitates the desorption of the olefin intermediate, which decreases the probability of its further hydrogenation. This predominantly decreases the rate of the complete hydrogenation and increases catalyst selectivity in the hydrogenation of structurally different substrates.

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REFERENCES

- 1. Borodzinski, A. and Bond, G.C., *Catal. Rev.*, 2006, vol. 48, p. 91.
- Ananikov, V.P., Khemchyan, L.L., Ivanova, Yu.V., Bukhtiyarov, V.I., Sorokin, A.M., Prosvirin, I.P., Vatsadze, S.Z., Medved'ko, A.V., Nuriev, V.N., Dil'man, A.D., Levin, V.V., Koptyug, I.V., Kovtunov, K.V., Zhivonitko, V.V., Likholobov, V.A., et al., *Russ. Chem. Rev.*, 2014, vol. 83, p. 885.
- 3. Nikolaev, S.A., Zanaveskin, L.N., Smirnov, V.V., Aver'yanov, V.A., and Zanaveskin, K.L., *Russ. Chem. Rev.*, 2009, vol. 78, p. 231.
- Bonrath, W., Medlock, J., Schütz, J., Wüstenberg, B., and Netscher, T., Hydrogenation: Overview, Karamé, I., Ed., InTech, 2012. http://www.intechopen.com/ books/hydrogenation/hydrogenation-in-the-vitaminsand-fine-chemicals-industry-an-overview.
- 5. Ichimura, K., Chem. Rev., 2000, vol. 100, p. 1847.
- Halim, M., Samuel, I.D.W., Pillow, J.N.G., Monkman, A.P., and Burn, P.L., *Synth. Met.*, 1999, vol. 102, p. 1571.
- Furukawa, Sh., Yokoyama, A., and Komatsu, T., ACS Catal., 2014, vol. 4, p. 3581.
- Blaser, H.-U., Schnyder, A., Steiner, H., Rossler, F., and Baumeister, P., in *Handbook of Heterogeneous Catalysis*, Ertl, G., Knözinger, H., Schüth, F., and Weitkamp, J., Eds., Weinheim, Germany: Wiley– VCH, 2008, vol. 8, p. 3298.
- Ananikov, V.P., Galkin, K.I., Egorov, M.P., Sakharov, A.M., Zlotin, S.G., Redina, E.A., Isaeva, V.I., Kustov, L.M., Gening, M.L., and Nifantiev, N.E., *Mendeleev Commun.*, 2016, vol. 26, p. 365.
- Ananikov, V.P., Khokhlova, E.A., Egorov, M.P., Sakharov, A.M., Zlotin, S.G., Kucherov, A.V., Kustov, L.M., Gening, M.L., and Nifantiev, N.E., *Mendeleev Commun.*, 2015, vol. 25, p. 75.
- 11. Karunananda, M.K. and Mankad, N.P., J. Am. Chem. Soc., 2015, vol. 137, p. 14598.
- 12. Pei, G.X., Yan, LiuX., Wang, A., Lee, A.F., Isaacs, M.A., Li, L., Pan, X., Yang, X., Wang, X., Tai, Z., Wilson, K., and Zhang, T., *ACS Catal.*, 2015, vol. 5, p. 3717.
- 13. Tan, L., Wu, X., Chen, D., Liu, H., Menga, X., and Tang, F., *J. Mater. Chem. A*, 2013, vol. 1, p. 10382.
- 14. McCue, A.J., Gibson, A., and Anderson, J.A., *Chem. Eng. J.*, 2016, vol. 285, p. 384.
- Chinayon, S., Mekasuwandumrong, O., Praserthdam, P., and Panpranot, J., *Catal. Commun.*, 2008, vol. 9, p. 2297.
- Mashkovskii, I.S., Tkachenko, O.P., Baeva, G.N., and Stakheev, A.Yu., *Kinet. Catal.*, 2009, vol. 50, no. 50, p. 768.
- Zhou, H., Yang, X., Wang, A., Miao, Sh., Liu, X., Pan, X., Su, Y., Li, L., Tan, Y., and Zhang, T., *Chin. J. Catal.*, 2016, vol. 37, p. 692.
- Mashkovsky, I.S., Baeva, G.N., Stakheev, A.Yu., Vargaftik, M.N., Kozitsyna, N.Yu., and Moiseev, I.I., *Mendeleev Commun.*, 2014, vol. 24, p. 355.
- 19. Föttinger, K., Catalysis, 2013, vol. 25, p. 77.

- Armbrüster, M., Behrens, M., Föttinger, K., Friedrich, M., Gaudry, É., Matam, S.K., and Sharma, H.R., *Catal. Rev. Sci. Eng.*, 2013, vol. 55, p. 289.
- Studt, F., Abild-Pedersen, F., Bligaard, T., Sørensen, R.Z., Christensen, C.H., and Nørskov, J.K., *Science*, 2008, vol. 320, p. 1320.
- 22. Furukawa, S. and Komatsu, T., ACS Catal., 2017, vol. 7, p. 735.
- Zhou, H., Yang, X., Li, L., Liu, X., Huang, Y., Pan, X., Wang, A., Li, J., and Zhang, T., *ACS Catal.*, 2016, vol. 6, p. 1054.
- 24. Yoshida, H., Zama, T., Fujita, S., Panpranot, J., and Arai, M., *RSC Adv.*, 2014, vol. 4, p. 24922.
- 25. Wang, Z., Yang, L., Zhang, R., Li, L., Cheng, Z., and Zhou, Z., *Catal. Today*, 2016, vol. 264, p. 37.
- Mashkovsky, I.S., Markov, P.V., Bragina, G.O., Baeva, G.N., Bukhtiyarov, A.V., Prosvirin, I.P., Bukhtiyarov, V.I., and Stakheev, A.Yu., *Kinet. Catal.*, 2017, vol. 58, p. 471.
- Markov, P.V., Bragina, G.O., Baeva, G.N., Tkachenko, O.P., Mashkovskii, I.S., Yakushev, I.A., Kozytsyna, N.Yu., Vargaftik, M.N., and Stakheev, A.Yu., *Kinet. Catal.*, 2015, vol. 56, p. 591.
- Spee, J., Boersma, J., Meijer, M.D., Slagt, M.Q., van Koten, G., and Geus, J.W., *J. Org. Chem.*, 2001, vol. 66, p. 1647.
- 29. Mashkovsky, I.S., Markov, P.V., Bragina, G.O., Tkachenko, O.P., Yakushev, I.A., Kozitsyna, N.Yu., Vargaftik, M.N., and Stakheev, A.Yu., *Russ. Chem. Bull.*, 2016, vol. 65, no. 2, p. 425.
- Domínguez-Domínguez, S., Berenguer-Murcia, A., Cazorla-Amorós, D., and Linares-Solano, A., *J. Catal.*, 2006, vol. 243, p. 74.
- Karakhanov, E.A., Aksenov, I.A., Kardashev, S.V., Maksimov, A.L., Putilin, F.N., Shatokhin, A.N., and Savilov, S.V., *Appl. Catal.*, *A*, 2013, vols. 464–465, p. 253.
- Marin-Astorga, N., Alvez-Manoli, G., and Reyes, P., J. Mol. Catal. A: Chem., 2005, vol. 226, p. 81.
- 33. Jung, A., Jess, A., Schubert, T., and Schütz, W., *Appl. Catal.*, *A*, 2009, vol. 362, p. 95.
- 34. Segura, Y., López, N., and Pérez-Ramírez, J., *J. Catal.*, 2007, vol. 247, p. 383.
- Teschner, D., Borsodi, J., and Wootsch, A., *Science*, 2008, vol. 320, p. 86.
- Vilé, G., Almora-Barrios, N., Mitchell, Sh., Lóopez, N., and Pérez-Ramírez, J., *Chem. Eur. J.*, 2014, vol. 20, p. 5926.
- Markov, P.V., Bragina, G.O., Baeva, G.N., Tkachenko, O.P., Mashkovskii, I.S., Yakushev, I.A., Vargaftik, M.N., and Stakheev, A.Yu., *Kinet. Catal.*, 2016, vol. 57, no. 5, p. 617.
- Markov, P.V., Bragina, G.O., Baeva, G.N., Mashkovskii, I.S., Rassolov, A.V., Yakushev, I.A., Vargaftik, M.N., and Stakheev, A.Yu., *Kinet. Catal.*, 2016, vol. 57, no. 5, p. 625.
- 39. Rassolov, A.V., Markov, P.V., Bragina, G.O., Baeva, G.N., Krivoruchenko, D.S., Mashkovskii, I.S.,

Yakushev, I.A., Vargaftik, M.N., and Stakheev, A.Yu., *Kinet. Catal.*, 2016, vol. 57, no. 6, p. 859.

- Osswald, J., Giedigkeit, R., Jentoft, R.E., Armbrüster, M., Girgsdies, F., Kovnir, K., Ressler, T., Grin, Yu., and Schlögl, R., *J. Catal.*, 2008, vol. 258, p. 210.
- Armbrüster, M., Kovnir, K., Behrens, M., Teschner, D., Grin, Yu., and Schlögl, R., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 14745.
- 42. Holzapfel, H.H., Wolfbeisser, A., Rameshan, C., Weilach, C., and Rupprechter, G., *Top. Catal.*, 2014, vol. 57, p. 1218.
- Gabasch, H., Knop-Gericke, A., Schlögl, R., Penner, S., Jenewein, B., and Hayek, K., and Klötzer, B., *J. Phys. Chem. B*, 2006, vol. 110, p. 11391.
- 44. Palczewska, W., Adv. Catal., 1975, vol. 24, p. 245.
- García-Mota, M., Gómez-Díaz, J., Novell-Leruth, G., Vargas-Fuentes, C., Bellarosa, L., and Pérez-Ramírez, J., and López, N., *Theor. Chem. Acc.*, 2011, vol. 128, p. 663.
- 46. Caga, I.T., Shutt, E., and Winterbottom, J.M., *J. Catal.*, 1976, vol. 44, p. 271.
- 47. Aduriz, H.R., Bodnariuk, P., Coq, B., and Figueras, F., *J. Catal.*, 1991, vol. 129, p. 47.
- 48. Armbrüster, M., Behrens, M., Cinquini, F., Föttinger, K., Grin, Yu., Haghofer, A., Klötzer, B., Knop-Gericke, A., Lorenz, H., Ota, A., Penner, S., Prinz, J., Rameshan, C., Révay, Z., Rosenthal, D., et al., *ChemCatChem*, 2012, vol. 4, p. 1048.
- Ota, A., Armbrüster, M., Behrens, M., Rosenthal, D., Friedrich, M., Kasatkin, I., Girgsdies, F., Zhang, W., Wagner, R., and Schlögl, R., *J. Phys. Chem. C*, 2010, vol. 115, p. 1368.
- 50. Yang, B., Burch, R., Hardacre, C., Headdock, G., and Hu, P., *J. Catal.*, 2013, vol. 305, p. 264.
- 51. Tew, M.W., Emerich, H., and van Bokhoven, J.A., *J. Phys. Chem. C*, 2011, vol. 115, p. 8457.
- 52. Rodriguez, J., J. Phys Chem., 1994, vol. 98, p. 5758.
- 53. Araña, J., Homs, N., Sales, J., Fierro, J.L.G., and Ramirez de la Piscina, P., *Catal. Lett.*, 2001, vol. 72, p. 183.
- 54. Wowsnick, G., Teschner, D., Armbrüster, M., Kasatkin, I., Girgsdies, F., Grin, Yu., Schlögl, R., and Behrens, M., *J. Catal.*, 2014, vol. 309, p. 221.
- 55. Bond, G.C., *Metal-Catalysed Reactions of Hydrocarbons*, New York: Springer Science + Business Media, 2005.
- Markov, P.V., Bragina, G.O., Rassolov, A.V., Mashkovsky, I.S., Baeva, G.N., Tkachenko, O.P., Yakushev, I.A., Vargaftik, M.N., and Stakheev, A.Yu., *Mendeleev Commun.*, 2016, vol. 26, p. 494.
- 57. Chin, Y.H., Dagle, R., Hu, J.L., Dohnalkova, A.C., and Wang, Y., *Catal. Today*, 2002, vol. 77, p. 79.
- Mitsudome, T., Takahashi, Y., Ichikawa, S., Mizugaki, T., Jitsukawa, K., and Kaneda, K., *Angew. Chem., Int. Ed. Engl.*, 2013, vol. 52, p. 1481.
- 59. Niu, M., Wang, Y., Li, W., Jiang, J., and Jin, Z., *Catal. Commun.*, 2013, vol. 38, p. 77.

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