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# Investigation of the State of Active Component in $Pd/Ga_2O_3$ and $Pd/In_2O_3$ Catalysts of Liquid-Phase Hydrogenation of Acetylene into Etylene

N. S. SMIRNOVA<sup>1</sup>, D. A. SHLYAPIN<sup>1</sup>, O. V. PROTASOVA<sup>1</sup>, M. V. TRENIKHIN<sup>1</sup>, T. I. GULYAEVA<sup>1</sup>, E. YU. GERASIMOV<sup>2</sup>, L. S. KIBIS<sup>2</sup>, N. B. SHITOVA<sup>1</sup>, D. I. KOCHUBEY<sup>2</sup> and P. G. TSYRUL'NIKOV<sup>1</sup>

<sup>1</sup>Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences, UI. Neftezavodskaya 54, Omsk 644040 (Russia)

E-mail: everinflame@gmail.com

<sup>2</sup>Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

#### Abstract

Catalysts of liquid-phase hydrogenation of acetylene deposited on the oxides of aluminium, gallium, and indium were studied. According to the results of catalytic tests and examination using the physical methods, decoration of the active component by partially reduced support is observed in  $Pd/Ga_2O_3$  and  $Pd/In_2O_3$  catalysts. An increase in the atomic catalytic activity for the samples deposited on gallium and indium oxides can be connected with the change of the electron density of the active component or with the formation of bimetallic phases.

Key words: liquid-phase hydrogenation of acetylene, EXAFS, XPES, TCD, chemisorption of CO,  $Pd/Ga_2O_3$ ,  $Pd/In_2O_3$ 

#### INTRODUCTION

Problem connected with natural gas and associated petroleum gas processing into more valuable products is urgent. One of the promising ways to solve these problems [1-3] is the GTL (gas-to-liquid) technology proposed by Synfuels International, Inc. (the USA) [4]. This technology is based on obtaining acetylene through oxidative pyrolysis of natural gas, subsequent selective hydrogenation of acetylene to form ethylene, and oligomerization of the latter leading to the components of motor fuel. It was proposed to carry out acetylene hydrogenation in the liquid phase because it is highly exothermal [5]. Among the catalysts for this process, one of the most efficient ones is supported palladium modified with the elements of IIIA group - indium and gallium [4-7].

Investigation of the intermetallic phases of palladium and gallium showed that at least three compounds of nine known for this system -PdGa, Pd<sub>3</sub>Ga<sub>7</sub> and Pd<sub>2</sub>Ga - may act as highly selective catalysts of gas-phase acetylene hydrogenation to form ethylene [8-11]. So, gallium is likely to cause modifying action. It is also known that Pd/Ga<sub>2</sub>O<sub>3</sub> and Pd/In<sub>2</sub>O<sub>3</sub> catalysts exhibit activity and are selective in reactions participated by hydrogen (synthesis of methanol from CO<sub>2</sub> and H<sub>2</sub>, hydrogenation of acetonitrile into ethyl amine) [12-14], and improvement of their catalytic properties is connected with redistribution of the electron density of palladium as a consequence of the interaction with the support in reducing atmosphere.

The goal of our work was to study the interaction of palladium with modifying oxides  $Ga_2O_3$  and  $In_2O_3$  in reducing atmosphere. The

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known catalyst of acetylene hydrogenation Pd/  $Al_2O_3$  was used as the reference for comparison [15–17].

#### EXPERIMENTAL

#### Preparation of supports

The granules of initial  $Al_2O_3 2.0-2.5$  mm in size (kh. ch. grade,  $S_{BET} = 270 \text{ m}^2/\text{g}$ ) were crushed, the resulting powder was sieved to obtain the fraction with particle size 0.07-0.09 mm, placed into corundum crucibles and calcined in a muffle furnace at a temperature of 900 °C for 10 h [18]. Commercially available reagents  $Ga_2O_3$  (os. ch. grade) and  $In_2O_3$  (kh. ch. grade) were used without additional purification.

#### Sample preparation

Samples containing 1 mass % Pd supported on  $Al_2O_3$ ,  $Ga_2O_3$  and  $In_2O_3$  were synthesized through impregnation of the support by the aqueous solution of  $Pd(NO_3)_2$  followed by evaporation of the solution on water bath and drying in the drying chamber at 120 °C for 2 h. After drying, the sample was reduced in hydrogen flow at a temperature of 200 °C for 3 h. The resulting samples were tested in liquidphase hydrogenation and investigated by means of physical methods.

#### Catalytic tests

The samples were tested in a shaken no-gradient flow reactor under the following conditions: reaction temperature 40 °C, gas mixture flow rate 100 mL/min, reactor swinging frequency  $7-8 \text{ s}^{-1}$ , the mass of catalyst portion was 10 mg, the volume of the solvent (*N*-methylpyrrolidone) was 8 mL. The composition of gaseous reaction mixture (vol. %): C<sub>2</sub>H<sub>2</sub> 4, H<sub>2</sub> 90, He 6 (balance). Experiment duration was 220 min.

Analysis of the initial reaction mixture and the mixture of reaction products was carried out with the help of a Khromos GKh-1000 chromatograph with a capillary column (immobile phase:  $SiO_2$ , working temperature: 60 °C) and flame ionization detector. Nitrogen was used as carrier gas. Acetylene conversion degree (X, %) and selectivity with respect to ethylene (S, %) were calculated from the areas of the corresponding peaks. Activity (W) as the rate of acetylene transformation per 1 g of the catalyst was calculated from the values of acetylene transformation degree. The dynamics *versus* the time of catalyst test was obtained for these values [19]. A comparative evaluation of the characteristics of different samples was obtained using the values from the region of the steady activity of the catalysts.

Comparing the atomic catalytic activity (ACA) values of the catalysts, we used the activities that corresponded to the achievement of 50 % transformation degree (X = 50 %). Activities were calculated from hydrogen transformation assuming that the reaction order with respect to C<sub>2</sub>H<sub>2</sub> is close to zero [15] and the stoichiometric ratio of acetylene and hydrogen in the reaction is 1 : 1.

#### X-ray phase analysis

The phase composition of oxide supports was determined by means of powder diffractometry using a Bruker D8 Advance diffractometer with copper  $K_{\alpha}$  radiation. The diffraction patterns were interpreted using the powder diffraction database the ICDD PDF-2 2006.

#### Determination of specific surface

The specific surface of initial supports was measured by means of BET procedure based on a single-point adsorption of nitrogen at 77 K.

#### Temperature-programmed reduction

The samples after drying at 120 °C were preliminarily annealed in air flow (60 mL/min) for 3 h at 350 °CC to obtain PdO/M<sub>2</sub>O<sub>3</sub>. Temperature-programmed reduction (TPR-H<sub>2</sub>) was carried out on a Micromeritics AutoChem II 2920 chemisorption analyzer with a heat conduction detector in a mixture of H<sub>2</sub>/Ar with the flow rate of 30 mL/min. The measuring cell was heated to 500 °C; heating rate was 10 °C/min.

# Determination of the disperse state of palladium from CO chemisorption

To determine the disperse state of palladium, we used pulsed chemisorption of CO. Investigation was carried out with a Micromeritics AutoChem II 2920 analyzer. Before experiments, the samples were reduced in the flow of 10 % H<sub>2</sub>/Ar at 200 °C for 30 min. Chemisorption was carried out after sample cooling in the inert gas to room temperature. A mixture of 10 vol. % CO–He was admitted in pulses at equal time intervals into the flow of the inert carrier gas (helium). Dispersity and apparent particle size were calculated taking into account linear chemisorption of CO on palladium (stoichiometric coefficient CO/Pd = 1 : 1).

#### Transmission electron microscopy

Electron microscopic studies of the samples were carried out using a JEM-2100 JEOL electron microscope (accelerating voltage 200 kV, resolution over the lattice 0.145 nm) with an INCA-250 EDX (Oxford Instruments). Suspensions of samples in alcohol were preliminarily subjected to ultrasonic dispersing (UZDN-2T) followed by deposition on carbon substrate fixed on a copper mesh.

Calibration of the linear size for the measurement of particle diameters was carried out over the crystal lattice of gold particles. The error of measurements of the linear size in electron microscopic images did not exceed 0.02 nm.

#### EXAFS spectroscopy

The EXAFS spectra of the *K* edge of palladium absorption were recorded at the EXAFS spectroscopy station of the Siberian Centre for Synchrotron and Terahertz Radiation (Institute of Nuclear Physics, Novosibirsk). The spectra were obtained using the synchrotron radiation; the energy of electrons in the VEPP-3 storage was equal to 2 GeV, and current strength was 70 mA. Split Si (111) crystal was used as a monochromator. All the spectra were recorded in the fluorescence mode with a step of 2.5 eV. The signal from the sample was recorded with the help of a scintillation detector operating in the current mode.

The recorded spectra were treated using Viper software according to a standard procedure [20]. The spectra were processed as a  $k^2\chi(k)$  function within wavenumber range k = 2.50-12.00 Å<sup>-1</sup>. Elimination of the back-ground was carried out by means of extrapolation of the pre-edge absorption region into the EXAFS region by Victorin polynomials. To calculate the smooth part of absorption coefficient, approximation based on three cubic smoothing spline functions was used. The point of inflection at the edge of absorption was used as the initial point  $E_0$  of EXAFS spectrum.

FEFF-7 program was used to obtain quantum chemical data necessary for the calculation of structural parameters [21]. The data on the structure of compounds were taken from the ICSD database [22]. Additionally, the reference spectrum of the K edge of Pd absorption in palladium foil was recorded.

#### X-ray photoelectron spectroscopy

The spectra were recorded using an ES 300 XPE spectrometer of Kratos Analytical Ltd. (UK) in the mode of operation of the X-ray tube  $13 \text{ kV} \times 13 \text{ mA}$ , which corresponds to the dissipation power of X-ray radiation 170 W. The  $K_{\alpha}$  line of aluminium with photon energy of 1486.6 eV was used as the primary radiation. The samples after preliminary grinding in a jasper mortar were applied onto the prismatic holder with the help of double-sided conducting adhesive tape. To determine the electronic state of Pd, the spectra of the basic photoelectron lines of palladium were obtained with the sweep step of 0.1 eV at the constant transmission energy of the analyzer HV = 25 eV. Carbon C 1s line with its bonding energy accepted to be 284.8 eV was accepted as the calibration reference for all the samples.

Decomposition of the spectra into components, smoothing and normalization were carried out with the help of the original software package XPSCalc which was previously tested with a number of various systems [24–26].

### **RESULTS AND DISCUSSION**

#### Characterization of supports

According to the XPA data,  $Al_2O_3$  is a mixture of  $\theta$ -Al\_2O\_3 (~22 %),  $\delta$ -Al\_2O\_3 (~23 %) and  $\eta$ -Al\_2O\_3 (~55 %) phases. Specific surface of Al\_2O\_3 was 100 m²/g. According to XPA data, the Ga\_2O\_3 sample contains only one (the most stable) modification  $\beta$ -Ga\_2O\_3. Indium oxide sample represents the most stable cubic modification c-In\_2O\_3. Specific surface values of the supports were determined according to BET procedure: 14 and 5 m²/g for  $\beta$ -Al\_2O\_3 and c-In\_2O\_3, respectively.

#### Catalytic tests of prepared samples

Catalysts containing 1 mass % palladium on the oxides of gallium, indium and aluminium were tested in the reaction of liquid-phase hydrogenation of acetylene under identical conditions in order to determine their characteristics. Test results are presented in Table 1.

One can see that the selectivity with respect to ethane is close to zero for all the catalysts. The samples deposited on aluminium and gallium oxides are comparable with each other in their catalytic properties. The highest acetylene transformation degree (45 %) was observed for the sample deposited on Al<sub>2</sub>O<sub>3</sub>, and the minimal one (8 %) was observed for the sample deposited on In<sub>2</sub>O<sub>3</sub>. For Pd/Ga<sub>2</sub>O<sub>3</sub>, the maximal selectivity among the samples of this series was established (56 %). In view of the low acetylene transformation degree for  $Pd/In_2O_3$  (8 %), it was impossible to estimate the selectivity with respect to each product with the necessary accuracy, so the weighted portion of the sample was increased by a factor of 5. According to the data shown in Table 1, for  $Pd/In_2O_3$  at X = 30 % the selectivity with respect to ethylene is 53 %.

In spite of the substantial difference in the values of specific surface of Al<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> (100 and 14  $m^2/g$ , respectively, see Table 1), catalysts on these supports are characterized by comparable values of acetylene transformation degree. The absence of external- and internaldiffusion kinetic limitations for the samples under study was established in preliminary experiments. So, close activity and selectivity may be due to the redistribution of the electron density of palladium as a consequence of the interaction with  $Ga_2O_3$  or the presence of less dispersed but more active phases in the Pd/  $Ga_2O_3$  sample. It is known that palladium on gallium oxide is able to form bimetallic compounds as a result of reduction; according to literature data, these bimetallic compounds are more active in acetylene hydrogenation than the catalysts composed of supported metal palladium [9-11, 27]. The formation of intermetallic compounds during reduction is also characteristic of the Pd/In<sub>2</sub>O<sub>3</sub> system, but the data on their catalytic activity in acetylene hydrogenation are still absent. To test the above assumption, we studied the catalysts using the physical methods.

#### Temperature-programmed reduction of catalysts

The results of the investigation of  $1 \% \text{Pd}/\text{Al}_2\text{O}_3$ ,  $1 \% \text{Pd}/\text{Ga}_2\text{O}_3$  and  $1 \% \text{Pd}/\text{In}_2\text{O}_3$  samples are presented in Fig. 1.

According to the data reported in [28], the reduction of palladium oxide by hydrogen to form metal palladium proceeds at temperatures close to room temperature. Sharp inversion peaks observed for the samples  $Pd/Al_2O_3$  and  $Pd/Ga_2O_3$  at a temperature of 72 and 61 °C

TABLE 1

Specific surface of the supports and the catalytic properties of  $Pd/M_2O_3$  samples (M = Al, Ga, In)

Samples	Weighed	$S_{\rm BET}, {\rm m}^2/{\rm g}$	Acetylene transformation	Selectivity (S), %		
	portion, mg		degree (X), $\%$	$C_2H_6$	$C_2H_4$	C <sub>4</sub>
Pd/Al <sub>2</sub> O <sub>3</sub>	10	100	45	0	48	52
$Pd/Ga_2O_3$	10	14	35	0	56	43
$Pd/In_2O_3$	10	5	8	-	-	_
$Pd/In_2O_3$	50	5	30	0	53	46

relate to desorption of hydrogen adsorbed on palladium surface because it is known that this process takes place within temperature range 40-100 °C [11, 28, 29]. A broad peak with the maximum at 146 °C observed for Pd/Al<sub>2</sub>O<sub>3</sub> presumably corresponds to the reduction of palladium oxide particles strongly bound with the support [30]. The TCD curve for the Pd/Ga<sub>2</sub>O<sub>3</sub> sample has a broad peak with not very high intensity, with the maximum at 270 °C, which may correspond to the formation of intermetallic compound Pd<sub>2</sub>Ga [11, 31].

In the case of  $Pd/In_2O_3$  catalyst, no peaks similar to  $Pd/Al_2O_3$  and  $Pd/Ga_2O_3$  were detected. Hydrogen absorption at a temperature above 400 °C is connected with the partial reduction of indium oxide [32]. The data obtained can be explained by the reduction of  $In_2O_3$ , which is accompanied by palladium encapsulation by the partially reduced support.

### EXAFS spectroscopy

According to the data of EXAFS spectroscopy, in the case of  $Pd/Al_2O_3$  catalyst, palladium is present in the system exclusively as the metal (Fig. 2). This is indicated by the observed peaks corresponding to the first four coordination spheres of *fcc* palladium (Pd-Pd 2.73, 3.84, 4.77, 5.35 Å).

The major part of palladium in the Pd/ $Ga_2O_3$  catalyst sample is present in the metal state (Pd-Pd distance is equal to 2.73 Å). The presence of the peak corresponding to Pd-Ga



Fig. 1. TPR profiles of catalysts:  $1 - PdO/Al_2O_3$ , 2 - PdO/Ga<sub>2</sub>O<sub>3</sub>, 3 - PdO/In<sub>2</sub>O<sub>3</sub>.

distance equal to 2.55 Å allows one to assume that a small part of Pd forms nonstoichiometric inhomogeneous alloy with gallium, reduced due to the effect of hydrogen spill over from palladium. The possibility of alloy formation was demonstrated in [33].

Modelling of the spectrum for the K edge of palladium absorption in  $Pd/In_2O_3$  catalyst shows the presence of two Pd-Pd distances (2.76 and 3.88 Å) corresponding to the distances in metal palladium. The distance equal to 4.5 Å can be related only to the Pd-In distance because the attempts to simulate this peak through the Pd-Pd distance leads to the negative coordination numbers. In this system, similarly to the previously considered system Pd/Ga<sub>2</sub>O<sub>3</sub>, partial reduction of indium oxide to suboxides or zero-valent indium due to hydrogen spillover from palladium particles can be assumed, too.

It is known that similarly to  $Pd/Ga_2O_3$  the reduction of  $Pd/In_2O_3$  results in the formation of intermetallic compounds [32]; however, in this case we did not succeed in detecting reliably the presence of the bimetallic phase.

Thus, the listed EXAFS data provide evidence in favour of the fact that comparable values of acetylene transformation degree for



Fig. 2. EXAFS spectra of the K edge of Pd absorption in samples:  $1 - 1 \% Pd/Al_2O_3$ ,  $2 - 1 \% Pd/Ga_2O_3$ ,  $3 - 1 \% Pd/In_2O_3$ .

the samples deposited on gallium and aluminium oxides are connected with the formation of the bimetallic phase in the case of  $Pd/Ga_2O_3$ . The distance of 4.93 Å for the  $Pd/Ga_2O_3$  sample and 4.50 Å for the  $Pd/In_2O_3$  sample may point to the decoration of palladium particles by supports. In the case of  $Pd/Ga_2O_3$  sample, a decrease in the available Pd surface is compensated by the appearance of some amount of active and selective palladium-gallium active centres. The low degree of acetylene conversion for the  $Pd/In_2O_3$  sample can be explained by blocking of palladium particles by the reduced support. In the case of  $Pd/Al_2O_3$ , encapsulation does not occur during the synthesis.

#### X-ray photoelectron spectroscopy

For the purpose of obtaining more detailed information about the state of the active component on catalyst surface, the samples of 1 %



Fig. 3. Spectrum of Pd 3d for samples:  $a = 1 \% \text{ Pd/Ga}_2\text{O}_3$ ,  $b = 1 \% \text{ Pd/In}_2\text{O}_3$ .

 $Pd/In_2O_3$  and 1 %  $Pd/Ga_2O_3$  were studied by means of XPE spectroscopy.

According to the data obtained, palladium is present in the Pd/Ga<sub>2</sub>O<sub>3</sub> sample in the form of metal palladium and oxide (Fig. 3, a). Intense doublet with  $E_{\rm b}$  (Pd  $3d_{5/2}$ ) = 334.8 eV is likely to relate to metal palladium clusters. The value of bonding energy (334.8 eV) is somewhat lower than the known value for  $Pd^0$  (335.0-335.2 eV) [34, 35]. The shift to smaller binding energy values may be due to partial decoration of palladium particles by the support, which causes the appearance of additional effects of recharging [24]. Less intense doublet is characterized by binding energy equal to 336.9 eV, which is typical for palladium oxide PdO [36, 37]. One also cannot exclude that it may be due to the presence of the joint phase of palladium and gallium like  $PdGa_xO_y$  containing Pd-O bonds, which is formed at the boundaries of the contacts of metal palladium particles and gallium oxide.

The XPE spectrum of palladium Pd 3*d* for Pd/In<sub>2</sub>O<sub>3</sub> is shown in Fig. 3, *b*. The state of palladium in the Pd/In<sub>2</sub>O<sub>3</sub> sample may be described by one doublet with  $E_{\rm b}$ (Pd 3*d*<sub>5/2</sub>) = 334.7 eV. This line is almost ideally described by Dognac–Sandgick [38], which points to the metal nature of this peak. A small shift to smaller binding energy values with respect to the peak of metal palladium can also be due to decoration of some palladium particles by indium oxide.

So, the data of XPES, similarly to EXAFS data, confirm our assumption concerning palladium blocking by the support in both samples.

## Investigation of $Pd/Al_2O_3$ , $Pd/Ga_2O_3$ and $Pd/In_2O_3$ by means of TEM

In the micrographs taken with the help of transmission electron microscope (Fig. 4, *b*), gray-contrast particles correspond to aluminium oxide, while darker ones correspond to supported palladium particles. According to the results of TEM, the active component is present in the 1 % Pd/Al<sub>2</sub>O<sub>3</sub> catalyst as solitary rounded particles and as agglomerates. The average size of palladium particles is 3.4 nm. The histogram of particle size distribution has two maxima corresponding to the ranges 2-2.5 and 4-4.5 nm



Fig. 4. Histogram of Pd particle size distribution (a) and the TEM data (b) for the  $1 \% Pd/Al_2O_3$  sample.

(see Fig. 4, a). This bimodal distribution of palladium particles may be connected either with the complicated phase composition of the support or with the processes that take place during the application of the active component or drying.

Similarly to  $Pd/Al_2O_3$ , the active component is present in the 1 %  $Pd/Ga_2O_3$  sample as agglomerates and solitary particles (Fig. 5, b). Because of the close values of the lattice parameters of metal palladium and palladium-gallium intermetallides, it is impossible to answer unambiguously whether the particles are composed of palladium or the interaction-related phase (alloy or intermetallic compound). The average particle diameter is equal to 2.9 nm, while the major part of the particles is characterized by the size less than 2.5 nm (see Fig. 5, *a*). Darker regions in comparison with the surrounding support (halo) are observed around some parti-



Fig. 5. Histogram of Pd particle size distribution (a) and the TEM data (b) for the  $1 \% Pd/Ga_2O_3$  sample.

cles, which can be an evidence of Pd decoration by partially reduced gallium oxide.

TEM investigation of the 1 % Pd/In<sub>2</sub>O<sub>3</sub> sample reduced at 200 °C showed that it is characterized by a broad particle size distribution from 2 to 12 nm, and the average particle size is 5.7 nm (Fig. 6, a). Palladium particles are surrounded by a thin layer of indium oxide (see Fig. 6, b). It is known that indium oxide particles located near palladium are able to render or accept oxygen readily [39]. So, at the stage of catalyst reduction palladium particles may be decorated with a thin layer of  $In_2O_3$  [39] till complete coating. Palladium particles are blocked up with partially reduced support, which may explain relatively low acetylene conversion degree for this sample in comparison with Pd/  $Ga_2O_3$  and  $Pd/Al_2O_3$  in the liquid-phase acetylene hydrogenation under similar conditions.



Fig. 6. Histogram of Pd particle size distribution (a) and the TEM data (b) for the  $1 \% Pd/In_2O_3$  sample.

Thus, the results of TEM are in complete agreement with EXAFS, XPES data and the results of catalytic tests: blocking of the active component by the support is observed in  $Pd/Ga_2O_3$  and  $Pd/In_2O_3$  samples; in the case of the palladium-indium sample blocking is almost complete.

# Determination of dispersity from CO chemisorption

Results of thee examination of the catalysts using the physical methods point to the presence of some amount of the bimetallic phase in Pd/Ga<sub>2</sub>O<sub>3</sub> and different extent of active component blocking in Pd/Ga<sub>2</sub>O<sub>3</sub> and Pd/ In<sub>2</sub>O<sub>3</sub> samples. In this connection, it is necessary to determine the amount of palladium available for reaction and the atomic catalytic activity (ACA) for all the samples. The data on dispersity and the size of the particles of the active component obtained by means of TEM and CO chemisorption, as well as calculated ACA values (reduced to acetylene conversion degree X = 50 % for all the samples) are presented in Table 2.

The average size of palladium particles determined using different methods are close to each other only for the  $Pd/Al_2O_3$  catalyst (3.4 and 4.4 nm). For the samples deposited on gallium and indium oxides, the parameters obtained by means of transmission electron microscopy and CO chemisorption differ from each other by a factor of 3.4 and 10.7 times, respectively. This substantial deviation is the evidence of the sorption of much smaller amount of CO on palladium surface than the value expected from the data on the size of palladium particles obtained by means of TEM. This is additional confirmation of active component blocking by the support. However, one cannot exclude the situation when a change of the stoichiometric factor of CO sorption on Pd occurs as a consequence of the change of phase composition (the formation of bimetal compounds) and/or electronic state of the active component on catalyst surface because the sample Pd/ Ga<sub>2</sub>O<sub>3</sub> contains along with metal palladium also a small amount of the palladium-gallium phase. In particular, CO molecule may get sorbed on metal palladium particle either in the linear form (CO/Pd = 1 : 1) or in the bridging form (CO/Pd = 1 : 1)Pd = 1 : 2). Stronger forms of CO sorption are also known (CO/Pd = 1 : 3) [31, 40]. For small

TABLE 2

Palladium particle size and calculated ACA values for Pd/M2O3 catalysts

Samples	W, mL of $C_2H_2/(min \cdot g_{cat})$	Averag TEM	e Pd particle size, nm CO	Pd dispersity, from CO chemisor	ACA, $s^{-1}$ rption, %
Pd/Al <sub>2</sub> O <sub>3</sub>	167	3.4	4.4	25	5.8
$Pd/Ga_2O_3$	73	2.9	9.9	11	6.1
$Pd/In_2O_3$	15	5.7	61.1	2	9.5

(<5 nm) palladium particles, the stoichiometric factor is accepted to be unity [40]. On the other hand, it was shown in [31] for the Pd/Ga<sub>2</sub>O<sub>3</sub> catalyst that CO molecules are sorbed on the active component (bimetal phase Pd<sub>2</sub>Ga) also mainly in the linear form (CO/Pd = 1 : 1). So, substantial discrepancies between the average particle size values are most probably due to active component blocking by the support.

For the series of samples under investigation, the atomic catalytic activity reduced to the degree of acetylene conversion X = 50 %was calculated on the basis of the data on CO chemisorption. The ACA values for the samples deposited on  $Ga_2O_3$  and  $In_2O_3$  (6.1 and 9.5 s<sup>-1</sup>, respectively) turned out to be higher than for  $Pd/Al_2O_3$  (5.8 s<sup>-1</sup>). The ability of  $Ga_2O_3$  and  $In_2O_3$ to get reduced partially at relatively low temperature (200-300 °C) provides the formation of bimetal phases and palladium decoration. Decoration is likely to provide an increase in their contact with the support, so the electronic state of the active component changes. The formation of bimetal phases also favours the improvement and selectivity of the catalyst.

#### CONCLUSION

It was established as a result of the studies that the synthesis of Pd/Ga<sub>2</sub>O<sub>3</sub> and Pd/In<sub>2</sub>O<sub>3</sub> catalysts involves fragmentary (or almost complete in the case of Pd/In<sub>2</sub>O<sub>3</sub> sample) blocking of the active component by partially reduced support. Palladium blocking determines the lower degree of acetylene transformation for Pd/ Ga<sub>2</sub>O<sub>3</sub> (X = 35 %) and Pd/In<sub>2</sub>O<sub>3</sub> (X = 8 %) in comparison with the Pd/Al<sub>2</sub>O<sub>3</sub> sample (X = 45 %) tested under identical conditions. Higher selectivity of the Pd/Ga<sub>2</sub>O<sub>3</sub> catalyst with respect to ethylene (56 %) in comparison with the sample on aluminium oxide (48 %) is connected with the formation of the joint palladium-gallium phase.

Calculated atomic catalytic activity values for  $Pd/Ga_2O_3$  (6.1 s<sup>-1</sup>) and  $Pd/In_2O_3$  (9.5 s<sup>-1</sup>) are higher than the value for  $Pd/Al_2O_3$  (5.8 s<sup>-1</sup>), which is the evidence of the positive modifying effect of gallium and indium oxides on palladium.

#### REFERENCES

- 1 Yapaskurt L. L., Miner. Res. Rossii. Ekon. Upravl., 1 (2006) 1.
- 2 Braginskiy O. B., Mirovaya Neftekhimicheskaya Promyshlennost', Nauka, Moscow, 2003, p. 556.
- 3 Knizhnikov A. Yu., Pusenkova N. N., Ekologiya i Energetika: Mezhdunar. Kontekst, 1 (2009) 1.
- 4 US Pat. No. 7692051 B2, 2010.
- 5 URL: http://www.synfuels.com (19.11.2012).
- 6 US Pat. No. 0021638A1, 2007.
- 7 US Pat. No. 0217781A1, 2011.
- Shao L., Zhang W., Armbruster M., Teschner D., Girgsdies F., Zhang B., Timpe O., Friedich M., Su D. S., Schlogl R., Angew. Chem. Int. Ed., 50, 43 (2011)10231.
  Osswald J., Kovnir K., Armbruster M., Giedigkeit R., Jentoft R. E.,Wild U., Grin Yu., Schlogl R., J. Catal., 258, 1 (2008) 219.
- 10 Ota A., Armbruster M., Behrens M., Rosenthal D., Friedrich M., Kasatkin I., Girgsdies F., Zhang W., Wagner R., Schlogl R., J. Phys. Chem. C, 115, 4 (2010) 1368.
- 11 Li L, Zhang B, Kunkes E, Fottinger K, Armbruster M, Su, D. S., Wei W., Schlogl R., Behrens M., *ChemCatChem.*, 4, 11 (2012) 1764.
- 12 Collins S. E., Baltanás M.A., Bonivardi A. L., J. Catal., 226, 2 (2004) 410.
- 13 Iwasa N., Yoshikawa M., Arai M., Phys. Chem. Chem. Phys., 4, 21 (2002) 5414.
- 14 Iwasa N., Yamamoto O., Tamura R., Nishikubo M., Takezawa N., Catal. Lett., 62, 2 (1999) 179.
- 15 Borodzicski A., Cybulski A., Appl. Catal. A: Gen., 198, 1-2 (2000) 51.
- 16 Vincent M. J., Gonzalez R. D., Appl. Catal. A: Gen., 217, 1-2 (2001) 143.
- 17 Komhom S., Praserthdam P., Mekasuwandumrong O., Panpranot J., React. Kinet. Catal. Lett., 94, 2 (2008) 233.
- 18 Kul'ko E. V., Ivanova A. S., Litvak G. S., Kryukova G. N., Tsybulya S. V., *Kinet. Katal.*, 45, 5 (2004) 754.
- 19 Shitova N. B., Shlyapin D. A., Afonasenko T. N., Kudrya E. N., Tsyrul'nikov P. G., Likholobov V. A., *Kinet. Katal.*, 52, 2 (2011) 259.
- 20 Kochubei D. I., EXAFS-Spektroskopiya Katalizatorov, Nauka, Novosibirsk, 1992.
- 21 URL: http://leonardo.phys.washington.edu/feff/ welcome (19.11.2012).

22 Inorganic Crystal Structure Database, 1998.

- URL: http://www.fiz-karlsruhe.de/icsd.html (10.10.2012).
- 23 Zanderna A. W. (Ed.), Methods of Surface Analysis, Elsevier, Amsterdam, 1975.
- 24 Slavinskaya E. M., Stonkus O. A., Gulyaev R. V., Ivanova A. S., Zaikovskii V. I., Kuznetsov P. A., Boronin A. I., *Appl. Catal. A: Gen.*, 401, 1–2 (2011) 83.
- 25 Podyacheva O. Yu, Ismagilov Z. R., Boronin A. I., Kibis L. S., Slavinskaya E. M. Noskov A. S., Shikina N. V., Ushakov V. A., Ischenko A. V., *Catal.Today*, 186, 1 ( 2012) 42.
- 26 Kibis L. S., Stadnichenko A. I., Koscheev S. V., Zaikovskii V. I., Boronin A. I., J. Phys. Chem. C, 116, 36 (2012) 19342.
- 27 Osswald J., Giedigkeit R., Jentoft R. E., Armbruster M., Girgsdies F., Kovnir K., Ressler T., Grin Yu., Schlogl R., J. Catal., 258, 1 (2008) 210.
- 28 Iwasa N., Takezawa N., Top. Catal., 22, 3 (2003) 215.
- 29 Boudart M., Hwang H. S., J. Catal., 39, 1 (1975) 44.

- 30 Gopinath R., Seshu B. N., Vinod K. J., Lingaiah N, Sai P. P., Catal. Lett., 120, 3 (2008) 312.
- 31 Haghofer A., Fottinger K., Girgsdies F., Teschner D., Knop-Gericke A., Schlogl R., Rupprechter G., J. Catal., 286 (2012) 13.
- 32 Neumann M., Rauchle K., Zhang A., Armbruster M., Reschetilowski W., 15th Int. Congress on Catalysis (Proceedings), Dechema, Munich, 2012.
- 33 Smirnova N. S., Shlyapin D. A., Mironenko O. O., Anoshkina E. A., Temerev V. L., Shitova N. B., Kochubey D. I., Tsyrul'nikov P. G., J. Mol. Catal. A: Chem., 358 (2012) 152.
- 34 Brun M., Berthet A., Bertolini J. C., J. Electron. Spectros. Relat. Phenom., 104, 1–3 (1999) 55.

- 35 Suhonen S., Valden M., Pessa M., Savimaki A., Harkonen M., Hietikko M., Pursiainen J., Laitinen R., Appl. Catal. A: Gen., 207, 1-2 (2001) 113.
- 36 Pillo Th., Zimmermann R., Steiner P., Hufner S., J. Phys. Condens. Matter, 9, 19 (1997) 3987.
- 37 Barr T. L., J. Phys. Chem., 82, 16 (1978) 1801.
- 38 Moulder J. F., Stickle W. W., Sobol P. E., Bomber K. D., Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer, Eden Praine, 1992, p. 72.
- 39 Lorenz H., Turner S., Lebedev O. I., Van Tendeloo G., Klotzer B., Rameshan C., Pfaller K., Penner S., Appl. Catal. A: Gen., 374, 1–2 (2010) 180.
- 40 Gurrath M., Kuretzky T., Boehm H. P., Okhlopkova L. B., Lisitsyn A. S., Likholobov V. A., Carbon, 38, 8 (2000) 1241.