

## ХИМИЯ ПОВЕРХНОСТИ ТВЕРДОФАЗНЫХ МАТЕРИАЛОВ

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### **Features of structural-phase state of Pd-Ag nanoparticles supported on silica gel**

*In this paper we synthesized and investigated mono- and bimetallic Pd-Ag nanoparticles supported on silica. The parameters of the crystal structure of supported Pd-Ag nanoparticles were investigated by X-ray diffraction (XRD). It was found that the addition of silver results in a distortion of the crystal lattice of palladium, which may indicate the interaction between the phases of silver and palladium on the support surface. Furthermore, the elemental composition of the formed metal particles was analyzed by energy dispersive spectroscopy (EDS) and by X-ray photoelectron spectroscopy (XPS).*

**Key words:** *Palladium alloys; bimetallic alloys; Pd-Ag nanoparticles; X-ray diffraction (XRD); X-ray photoelectron spectroscopy (XPS).*

Alloys based on palladium possess unique physical-mechanical and physical-chemical properties. This contributes to their wide application in various sectors of the chemical industry [1]. Palladium-based alloys are used as membrane materials, as they have the necessary set of functional properties: a good hydrogen permeability, high mechanical strength and thermal resistance in a gaseous environment. Palladium alloys are widely used in catalysis. Practical application of the system are bimetallic Pd-Cu, Pd-Ni, Pd-Ag, Pd-Au, Pd-Rh, Pd-Ru and al. [2].

Palladium refers to the VIIIA group of the D.I. Mendeleev's periodic table unfinished 4d-shell and has the properties typical of the group of transition elements. Like most of the elements palladium forms a complex system with a large number of chemical compounds. On the other hand, palladium dissolves well alloying metals, forming large areas of homogeneous solid solutions [3, 4]. In systems based on palladium the second forming-alloy metal elements are neighbors of palladium in the periodic table: cobalt, rhodium, iridium from VIIA subgroups, nickel and platinum from VIIIA subgroup (to which belongs palladium) and copper, silver and gold from the IB subgroup. These elements form

alloys with electronic structure close to palladium [5]. In the above systems, binary alloys based on palladium very well meet the conditions of formation of continuous series of solid solutions of metal compounds [3]:

- lattices forming the alloy elements of the same type (with the exception of Co);

- atomic similarity components forming compounds (proximity and size of the electronic structure of atoms);

- type of chemical bond in the compounds of the same.

Under these conditions, the mixing energy

$$w = U_{AB} - \frac{U_{AA} + U_{BB}}{2},$$

(where  $U_{AB}$ ,  $U_{AA}$ ,  $U_{BB}$  – the potential energy of interaction between the atoms of different sorts ( $AB$ ) and the same sorts ( $AA$  и  $BB$ ) respectively) is close to zero, which is a necessary condition for the formation of solid solutions [6].

Modern industrial catalysts are usually complex multicomponent systems, even when the two metal components forming the system have the same structural phase state [5]. Currently, active and stable catalysts based on supported noble metal particles, in particular palladium, are widely used in the chemical and petrochemical industries in various reaction such as a wide range of hydrogenation processes, cracking, polymerization, hydrotreating and oxidation. In complex catalytic processes are increasingly used systems based on nanoparticles bi- and polymetallic alloys [7]. A great interest in literature is given to Pd-Ag nanoparticles supported on different supports. Catalysts based on them are promising among bimetallic systems in selective hydrogenation reactions [8] and deep oxidation of CO [9]. Catalytic and adsorption properties of bimetallic systems are directly related to the structural-phase and the valence state of bimetallic Pd-Ag nanoparticles.

Interesting results related to this study were obtained by XPS for Ag [12–14], Pd [15–19] and Pd-Ag [20, 21] nanoparticles. For the supported metal nanoparticles some interesting effects can be observed (eg, asymmetry, chemical shift, broadening, etc.) in the photoelectron spectra, depending on the size of the particles (see [10–11] and references therein). In particular, the chemical shift 1–2 eV and a significant broadening of the peaks of the core levels were observed for small nanoparticles (2–3 nm in diameter) compared to the volume of the metal [12–19].

Based on the foregoing, this study show that the structure-phase and the valence state supported bimetallic particles are important parameters. The aim of the present paper was to study the structural phase state of mono- and bimetallic nanoparticles of palladium and silver, which are the active components of the catalysts Pd-Ag/SiO<sub>2</sub>. The nature of the interaction between palladium and silver on the surface of the support has been studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The research of structural and valence state of Pd-Ag bimetallic nanoparticles in catalysts supported on silica was performed and a comparison with the monometallic palladium and silver catalyst was done.

## Experimental part

### *Synthesis support*

Support  $\text{SiO}_2$  was prepared by sol-gel method using tetraethyl orthosilicate (TEOS) as the silicon oxide precursor, water as the solvent and concentrated nitric acid as the hydrolysis catalyst. The components were mixed in a volumetric ratio of  $\text{TEOS}:\text{H}_2\text{O}:\text{HNO}_3 = 12:12:1$  and stirred at room temperature for 1 hour. Then, the resulting sol was placed in a sealed container and allowed to gelation and maturation of the gel at  $50^\circ\text{C}$  for 3 days. The resulting gel was dried at  $50^\circ\text{C}$  for 15 hours and calcined at  $500^\circ\text{C}$  for 5 hours to remove residual organic substances and fixing structure of silica gel. The gel was then subjected to a hydrothermal treatment with aqueous ammonia at  $120^\circ\text{C}$  for 3 hours to change the pore structure – from a microporous to a mesoporous system [22]. Then the silica gel was dried to remove residual ammonia, and calcined at  $900^\circ\text{C}$  for 5 hours to fix the porous structure and reduce the amount of surface silanol groups [23].

### *Synthesis catalysts*

Palladium catalysts were synthesized by incipient wetness impregnation with an aqueous solution of tetrachloropalladium acid, which was obtained by dissolving palladium in a mixture of concentrated nitric and hydrochloric acid at a volume ratio of 1:3. The samples were then calcined in air at  $500^\circ\text{C}$  for 5 h. to complete palladium precursor decomposition. To obtain silver-containing catalysts, calcined samples of catalysts containing palladium were impregnated with an aqueous solution of silver nitrate. Finally, the samples were subjected to an oxidation treatment at  $500^\circ\text{C}$  to decompose the silver precursor. The quantitative characteristics of the synthesized samples with a variable ratio of Pd:Ag are shown in table 1.

Table 1

**The volume content of components in the samples (wt. %)**

| Element | Sample |             |             |     |
|---------|--------|-------------|-------------|-----|
|         | Pd     | Pd:Ag (1:1) | Pd:Ag (1:3) | Ag  |
| Pd      | 3.7    | 1.3         | 2.2         | 0.0 |
| Ag      | 0.0    | 1.4         | 5.8         | 7.0 |

### *Specific surface area*

Measurement of the specific surface area, pore volume and pore size distribution of support was carried out by using the method of low-temperature ( $-196^\circ\text{C}$ ) nitrogen adsorption in an automatic gas adsorption analyzer TriStar 3020 («Micromeritics», USA). The specific surface area was calculated by BET multipoint method with straightening adsorption isotherm in the range of  $P/P^0$  of

0.05 to 0.30. Pore size distribution was analyzed by the desorption branch of the isotherm adsorption-desorption of nitrogen by the method of Barrett Joyner Halenda (BJH). Prior to sorption measurements the samples were subjected to sorption thermal vacuum degassing processing at station VacPrep 061 («Micro-metrics», USA) at a pressure of 50 mTorr and a temperature of 200°C for 2 hours to remove the surface adsorbed water and other impurities from the sample.

### *X-ray analysis*

The study of the phase composition of synthesized catalysts was conducted using the method of X-ray diffraction (XRD). XRD patterns were obtained by powder diffractometer XRD 6000 («Shimadzu», Japan) using the  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a Ni filter. Recording conditions: scanning speed 4.0°/min, scan angle range of 10° to 85°, step scan 0.03°, tube voltage 40 kV, amperage 30 mA. The diffraction peaks of crystalline phases were processed using software POWDER CELL 2.4. The phase identification was carried out using a database PCPDFWIN on radiographs of the individual components. Calculation of interplanar spacings ( $d$ , Å) and crystal lattice parameters ( $a$ , Å) was carried out according to the Wulff-Bragg formula. The average crystallite size ( $D$ , nm), which equates to the areas of coherent scattering, was evaluated by Selyakov-Scherrer equation.

### *The elemental composition*

Photoelectron spectra of the samples were recorded using X-ray photoelectron spectrometer Escalab 250 (Thermo Scientific, USA) equipped with a combined source of ion-electron surface charge compensation. Samples were pressed, fixed on a double-sided copper tape and was then introduced into the chamber of the spectrometer. For each of the samples was recorded a panoramic range for elemental analysis, and then investigated the detailed spectra of the regions of interest (Pd3d, Ag3d, Si2p, O1s, C1s). For the elements of interest (Pd, Ag) the value of the pass energy was 20 eV to provide optimum energy resolution. Full spectrum of d- and p-levels have been processed using Gaussian and Lorentz functions, while optimizing the background. To determine the volume content of palladium and silver (to a depth of 2 microns) in the synthesized samples energy dispersive spectroscopy (EDS) was used. The primary electrons used for EDS were obtained by a field emission gun within the XPS spectrometer Escalab 250 (Thermo Scientific, USA).

## **Results and discussion**

The porous structure of the support was investigated by low-temperature nitrogen adsorption. On isotherm adsorption-desorption of nitrogen (Fig. 1a) there is a hysteresis loop in the relative pressure range from 0.9 to 1.0, indicating a mesoporous structure of silica gel with a predominance of pores larger

than 10 nm. From of the pore size distribution (Fig. 1b) we can derive that the synthesized silica has a characteristic pore size of 20–100 nm, with a low content of pores smaller than 10 nm. The use of macroporous silica gel as a support reduces the effects of the porous structure of the support on the particles size of the deposited active component. The specific surface area of the silica gel, as determined by multipoint BET method, was 65.3 m<sup>2</sup>/g with a pore volume of 0.31 cm<sup>3</sup>/g. Interactions between the Pd and Ag can lead to the formation of intermetallic compounds on the surface of the support [24], as well as solid solutions [25].

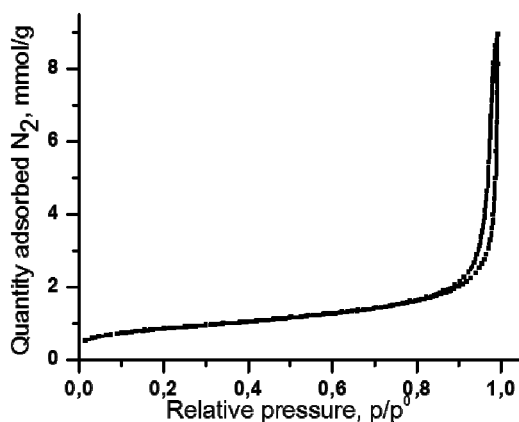


Fig. 1a. Adsorption-desorption isotherms of silica gel

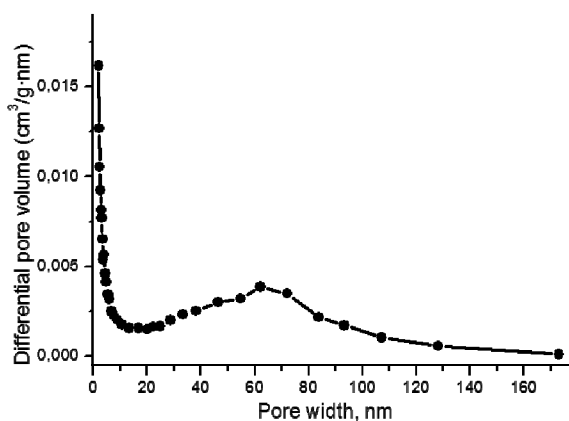


Fig. 1b. Differential pore size distribution of silica gel

Figure 2 a shows diffraction patterns for monometallic palladium (Pd), silver (Ag), and a mixed bimetallic Pd Ag nanoparticles (Pd:Ag (1:1), Pd:Ag (1:3)) catalysts supported on silica. For all diffractograms we detect the characteristic diffraction broad line from the amorphous support SiO<sub>2</sub> at angles 2θ of

15 to 35 with a maximum of ~22–23. For monometallic systems containing only nanoparticles of palladium (Pd) diffractogram have two peaks at angles  $2\theta$  40.00° (111) and 46.54° (200), which correspond to the phase of metallic palladium. A system comprising only nanoparticles of silver (Ag) has diffraction peaks at angles  $2\theta$  38.14° (111) and 46.23° (200), which is associated with the presence of metallic silver phase.

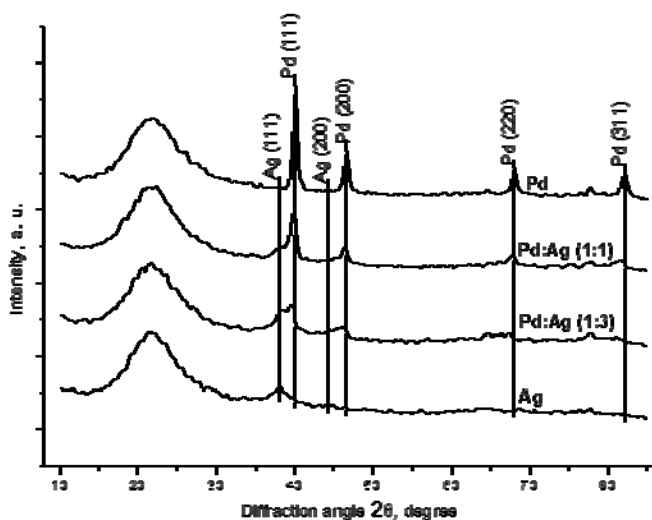


Fig. 2a. Diffractograms supported Pd-Ag nanoparticles reduced in  $H_2$  at 500°C

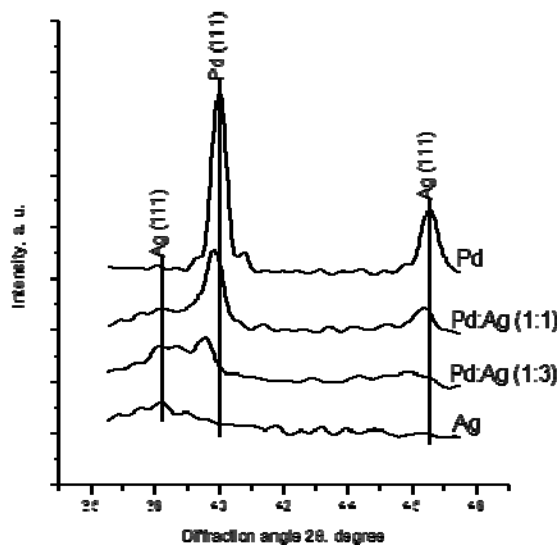


Fig. 2b. Fragments of diffractograms in the  $2\theta$  angles from 36° to 48°

In the case of bimetallic systems diffraction peaks, that are characteristic of pure metallic Pd and Ag, shift: those of palladium to smaller angles  $2\theta$  and those of silver to large angles  $2\theta$  (Fig. 2b). This is due to the distortion of the crystal lattice, which in turn is caused by interfacial interaction between the palladium and silver on the surface of the silica without the formation of solid solution, because in this case the diffraction maxima would have been located between the lines corresponding to pure Pd and Ag. Interaction between palladium and silver on the support surface can be associated with the formation of the interface Pd/Ag with possible partial atomic mixing.

Using the Selyakov-Scherrer equation were calculated average particle sizes of palladium and silver monometallic and bimetallic catalysts (Table 2). The average size of the crystallites of palladium and silver, estimated at 15 to 20 nm and 3 to 5 nm, respectively.

Table 2

**Characteristics of the crystal structure**

| Sample      | $d_{111}$ (Pd), Å | $a$ (Pd), Å | $D$ (Pd), nm | $d_{111}$ (Ag), Å | $a$ (Ag), Å | $D$ (Ag), nm |
|-------------|-------------------|-------------|--------------|-------------------|-------------|--------------|
| Pd          | 2.25              | 3.90        | 19.6         | —                 | —           | —            |
| Pd:Ag (1:1) | 2.26              | 3.91        | 16.0         | 2.32              | 4.02        | 3.2          |
| Pd:Ag (1:3) | 2.28              | 3.95        | 18.4         | 2.34              | 4.05        | 4.6          |
| Ag          | —                 | —           | —            | 2.36              | 4.09        | 3.5          |

$d_{111}$  – interplanar spacing;  $D$  – coherent scattering region (mean size);  $a$  – lattice constant.

Low intensity and broadened reflections of silver are associated with a small size (in the field detection limit of XRD method, see Table 2) and a low degree of crystallinity of the silver particles. While well-defined reflections, even while reducing its contents within the catalyst, for the palladium metal phase indicate the relatively large size of the particles of palladium (see Table 2) and a high degree of crystallinity of the formed particles on the support surface.

For all samples was carried out elemental analysis of the surface. The results are shown in Table 3. In all the samples was observed a contribution of pollution carbon. It is important to note, that in all samples the content of palladium at the surface is always considerably lower, than in the bulk, which can be explained by the predominant localization of silver on the surface [21], while palladium may be localized below silver on the support.

For silver, the chemical shift of the Ag3d-line for silver nanoparticles of 2 nm is reported to be about 0.6 eV [12], however, this value is highly dependent on the nature of the support. Peaks for silver nanoparticles having dimensions from 2 to 6 nm in diameter exhibit some degree of asymmetry, in contrast to the pure metal surfaces, the peaks of which are almost symmetrical. For the Pd-Ag nanoparticles significant negative shift in the binding energy (–0.7 eV) Ag3d-line core level in Pd-Ag samples, compared to metallic silver, which can be associated with the formation of Pd-Ag alloy and consequent charge transfer [20].

Table 3

Content of elements on the surface according to XPS

| Sample      | The elemental composition (wt.%) |     |
|-------------|----------------------------------|-----|
|             | Pd                               | Ag  |
| Pd          | 0.5                              | —   |
| Pd:Ag (1:1) | 0.2                              | 1.2 |
| Pd:Ag (1:3) | 0.2                              | 3.0 |
| Ag          | —                                | 5.0 |

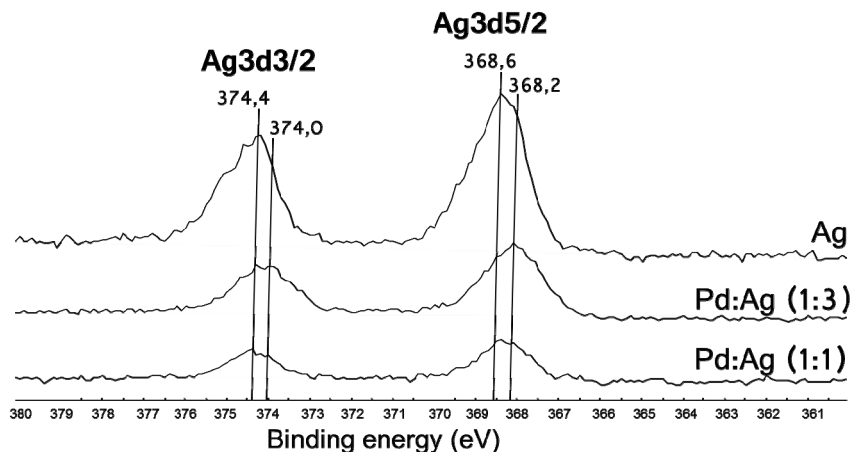


Fig. 3a. XPS spectra of the binding energy of the levels Ag3d3/2 and Ag3d5/2

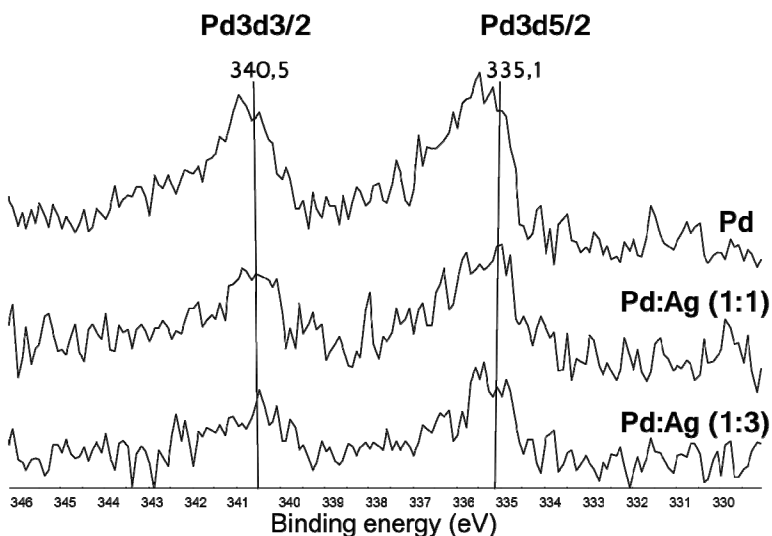


Fig. 3b. XPS spectra of the binding energy of the levels Pd3d3/2 and Pd3d5/2



For nanoparticles of palladium and palladium metal surfaces the photoelectron peaks are asymmetric [15–19]; in the case of small nanoparticles, depending on the support and the method use for preparation, the asymmetry of the peaks, according to some authors, is associated with the oxidation of the surface of the palladium nanoparticles that forms a non-stoichiometric oxide  $\text{PdO}_x$ . The chemical shift of  $\text{PdO}_x$  nanoparticle surface compared to the metal palladium reportedly amounts to 1.4 to 2.0 eV [15, 16, 19].

XPS spectra of silver samples of different composition are shown in Figure 3 a. For silver metal the binding energy levels of  $\text{Ag}3d_{5/2}$  and  $\text{Ag}3d_{3/2}$  are 368.3 eV and 374.3 eV, respectively. It is interesting to note that the position of the  $\text{Ag}3d$ -lines binding energy in the Pd-Ag samples are approximately 0.3–0.4 eV lower than for metallic silver, which is consistent with literature data [20]. We can conclude that in the synthesized samples are not observed the formation of solid solutions. The shift of 0.4 eV may be caused primarily to lower dispersion of silver nanoparticles and the formation of an interfacial interface Pd/Ag. The silver/ palladium ratio measured by XPS was larger than the one measured by global analysis (ICP) indicating that silver occupies the surface since it may form on top of the pre-formed palladium nanoparticles [21].

Figure 3b shows the XPS spectra of palladium samples of different composition. The noisy obtained spectra Pd3d is associated with low surface palladium content in the synthesized samples. As shown in Figure 3 b, with changes in the palladium content, the chemical shift was not detected in the spectra Pd3d. This may be due to the large amount of palladium nanoparticles in the synthesized samples, and with a low concentration of nanoparticles on the surface of the silica gel.

## Conclusions

In this paper we synthesized and investigated silver, palladium and Pd-Ag bimetallic nanoparticles supported on silica which can be used as catalysts for deep oxidation. It is found that in the bimetallic systems are not formed particles representing a bimetallic alloy. There is aggregation of silver particles and palladium, to form a wide interfacial interface between the two metal atoms. Silver particles are formed in a highly dispersed state. Bimetallic particles with a wide interface may be active in catalysis due to the division and reactions of parallel processes on each particle.

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### **Особенности структурно-фазового состояния Pd-Ag наночастиц, нанесенных на силикагель**

Сплавы на основе палладия обладают уникальными физико-химическими свойствами. Это способствует широкому использованию этих сплавов в различных отраслях химической промышленности. Катализаторы на основе палладиевых сплавов широко используются в катализе. Практическое применение находят сплавы в системах Pd-Cu, Pd-Ni, Pd-Ag, Pd-Au, Pd-Rh, Pd-Ru и др.

С большинством элементов палладий образует сложные системы с большим числом химических соединений. С другой стороны, палладий хорошо растворяет легирующие металлы, образуя значительные области твердых растворов. Бинарные сплавы на основе палладия очень хорошо соответствуют условиям образования непрерывных рядов твердых растворов для металлических соединений.

Используемые современной промышленностью катализаторы, как правило, являются сложными многокомпонентными системами, причем число компонентов в промышленных катализаторах часто весьма значительно. Уже при двух образующих систему компонентах структурно-фазовые состояния компонентов катализатора могут быть довольно сложными и разнообразными. Все чаще используют системы на основе наночастиц би- и полиметаллических сплавов.

Большой интерес уделяется Pd-Ag наночастицам, нанесенным на различные носители. Так, катализаторы на их основе являются одними из перспективных среди биметаллических систем в реакциях селективного гидрирования и глубокого окисления СО. Каталитические и адсорбционные свойства каталитических систем будут напрямую связаны со структурно-фазовым и валентным состоянием биметаллических Pd-Ag наночастиц. Исходя из вышесказанного, исследование особенностей структурно-фазового состояния и валентного состояния нанесенных биметаллических частиц является актуальным.

Целью настоящей работы являлось изучение структурно-фазового состояния моно- и биметаллических наночастиц палладия и серебра, нанесенных на силикагель, являющихся активными компонентами катализаторов Pd-Ag/SiO<sub>2</sub>. Характер взаимодействия между палладием и серебром на поверхности носителя, был изучен методами рентгенофазового анализа и рентгеновской фотоэлектронной спектроскопии. Выполнено исследование структурного и валентного состояния биметаллических Pd-Ag наночастиц в нанесенных на силикагель катализаторах. Проведено сравнение с монометаллическими палладиевыми и серебряными катализаторами.

В настоящей работе синтезированы и исследованы серебряные, палладиевые и биметаллические Pd-Ag наночастицы, нанесенные на силикагель, которые могут быть использованы в качестве катализаторов глубокого окисления. Установлено, что в биметаллической системе не образуются частицы, представляющие собой биметаллический сплав. Наблюдается агрегация серебряных и палладиевых частиц с образованием широкого межфазного интерфейса

между атомами двух металлов. Частицы серебра формируются в высокодисперсном состоянии. Биметаллические частицы с широким межфазным интерфейсом могут быть активными в катализе, что связано с разделением реакций и параллельными процессами на каждой частице.

**Ключевые слова:** сплавы палладия; биметаллические сплавы; Pd–Ag наночастицы; рентгенофазовый анализ; рентгеновская фотоэлектронная спектроскопия.

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