Conference paper

Elena V. Golubina, Tatiana N. Rostovshchikova, Ekaterina S. Lokteva*,
Konstantin I. Maslakov, Sergey A. Nikolaev, Tolganay B. Egorova, Sergey A. Gurevich,
Vladimir M. Kozhevin, Denis A. Yavsin and Anatoly Ye. Yermakov

Chlorobenzene hydrodechlorination on bimetallic catalysts prepared by laser electrodispersion of NiPd alloy

<https://doi.org/10.1515/pac-2018-0207>

Abstract: NiPd bimetallic systems were for the first time synthesized by laser electrodispersion (LED) of the Ni₇₇Pd₂₃ alloy target followed by the deposition of produced bimetallic particles on a TEM copper grid and alumina granules. Selective area energy-dispersive analysis confirms the bimetallic nature of NiPd particles deposited on a TEM copper grid. Their mean size is 1.0 nm according to TEM. XPS data demonstrate that under deposition on alumina granules (total metal content of 0.005 wt.%), nickel in bimetallic particles nearly completely oxidizes to Ni²⁺ species predominantly in the form of aluminate. At the same time major part of palladium (84 %) exists in Pd⁰ but oxidizes to Pd²⁺ (80 %) during 6 months storage in air. Both metals are deposited on the external surface of alumina granules and localized in the same areas. In situ reduction of both metals by H₂ in the catalytic cell of XPS spectrometer is hindered. Nickel is not reduced even at 450 °C, confirming the formation of NiAlO_x, whereas palladium is reduced at higher temperatures compared to a similar monometallic catalyst. Nevertheless, NiPd/Al₂O₃ catalyst is more efficient in gas-phase chlorobenzene hydrodechlorination at 150–350 °C than Ni/Al₂O₃ and even Pd/Al₂O₃, and much more stable. The difference may be caused by the formation of new active sites due to the contact between Pd⁰ and NiAlO_x-modified support, and the protective action of spinel reacting with HCl by-product.

Keywords: alumina; bimetallic catalyst; chlorobenzene; hydrodechlorination; ICGC-7; laser electrodispersion; nickel; NiPd alloy; palladium.

Introduction

As heterogeneous catalysts based on bi- and polymetallic nanocrystalline alloys are promising for the use in industrially important processes, the investigation of their catalytic action is very important for the development of fundamental concepts of catalysis [1–3]. A variety of methods of wet chemistry, such as impregnation, co-precipitation, ion exchange etc. are used for the preparation of supported metal-containing

Article note: A collection of invited papers based on presentations at the 7th International IUPAC Conference on Green Chemistry (ICGC-7), Moscow, Russia, 2–5 October 2017.

***Corresponding author: Ekaterina S. Lokteva**, Lomonosov Moscow State University, Moscow, Russia,
e-mail: e.lokteva@rambler.ru

Elena V. Golubina, Tatiana N. Rostovshchikova, Konstantin I. Maslakov, Sergey A. Nikolaev and Tolganay B. Egorova:
Lomonosov Moscow State University, Moscow, Russia

Sergey A. Gurevich, Vladimir M. Kozhevin and Denis A. Yavsin: Ioffe Physico-Technical Institute of RAS, St. Petersburg, Russia
Anatoly Ye. Yermakov: M. N. Miheev Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, Yekaterinburg, Russia; and Ural Federal University named after the first President of Russia B. N. Yeltsin, Yekaterinburg, Russia

catalysts [4–7]. These methods are cheap, convenient, and often well studied. The obvious advantages of ‘wet’ methods include fairly simple equipment and no restrictions on the nature of the catalytic support used. However, it is not always possible to achieve the desired dispersion, composition and appropriate loading of the catalytically active component, for example, nanoparticles of a catalytically active metal. As a result, the catalysts prepared by these methods do not fully realize the high potential inherent to the nature of the catalytically active component and support. Moreover, ‘wet’ synthesis is usually a multi-stage process that depends on many factors. They are not always reproducible and cause significant environmental impact. The development of novel ‘dry’ size-selective methods of producing nanoparticle of homogeneous composition remains an important problem.

In recent years an alternative way of producing nanoparticles from bulk metals using laser ablation into liquid has been attracting the increasing attention [8, 9]. ‘Dry’ physical top-down nanoparticle deposition methods are eco-friendly, and they can be used for ‘green’ one step synthesis of ligand-free nanoparticles for catalytic applications. But as the ‘wet’ chemistry methods, the most commonly used techniques of the laser ablation are unsuitable for the fabrication of densely packed layers of separated nanoparticles because nanoparticles closely-packed on the support surface tend to coagulate into larger aggregates. As a result, the size of metal nanoparticles usually increases with the deposition time or metal loading. Recently developed method of laser electrodispersion (LED) [5, 10], which produces amorphous nanoparticles that are unusually stable to aggregation, allows overcoming this difficulty. This method does not require the use of solvents or stabilizers. In contrast to the conventional laser ablation technique, in which particles are formed by the condensation of separate atoms, LED method is based on the melting of a metallic target to produce liquid metal drops and the cascade fission of such drops in the laser torch plasma. As a result, nanoparticles of the strictly definite size determined only by the electron work function of the metal are formed [10, 11]. A distinctive feature of this method is the production of core-shell catalysts in which size selected metal particles are uniformly distributed only on the outer surface of support granules [12]. These particles are very promising for catalysis due to their optimal size, availability to reagents and improved stability against sintering and poisoning [10]. Besides, the adsorption and redox properties of LED-produced metal particles differ from those prepared by traditional methods, which makes LED nanoparticles attractive for the synthesis of nanomaterials with new and unique properties [6, 12]. The activity of monometallic LED catalysts with low (<0.01 wt.%) metal content is several orders of magnitude higher in a wide range of reactions than that of supported catalysts prepared by classical ‘wet’ techniques [10, 13, 14]. The unusually high activity of LED catalysts is apparently attributed to the structure of nanoparticle coatings produced by this method. The key features of LED catalysts are the high specific surface area of the active component associated with the small particle size, the purity of LED particle surface and the distribution of particles over the outer surface of the support. As a result, even catalysts with a low metal content are characterized by the high surface particle density (more than 0.5 monolayer) and a large number of particle contacts with the neighboring particles and the support. These inter-particle and particle-support interfaces are crucial for heterogeneous catalysis [4, 15–17].

The choice of the active metals for the catalytic systems and the test reaction used in this work was dictated by several reasons. The hydrodechlorination (HDC) reaction ($\text{RCl} + \text{H}_2 \rightarrow \text{RH} + \text{HCl}$) is of great interest because it can be used to neutralize and recover chlorine-containing organic products without releasing dioxins, which are dangerous for the environment, and with the retention of the hydrocarbon part of RCl molecules [18, 19]. HDC catalysts usually contain transition metals, with Pd being the most active one and very efficient in activation of the molecular H_2 [20]. However, Pd catalysts are expensive and prone to deactivation. Ni provides a good alternative to Pd due to its significantly lower price. But at the same time, it deactivates much more easily. The loss of activity during long-term catalytic test can be caused by the agglomeration of metal nanoparticles, the oxidation of metal reacting with the inevitable by-product of HDC – hydrogen chloride, and the formation of carbon deposits on the surface of the active metal [21]. In fact, LED method proved its efficiency in mitigation of deactivation problem. Pd and Ni LED catalysts are less prone to chlorination in HDC conditions. But supporting of Ni nanoparticles on oxides (e.g. Al_2O_3) is accompanied by the strong interaction and encapsulation that cause a loss of potential activity, especially in the reaction

conditions [10, 12]. The well-known approach that helps to enhance the catalyst stability is the modification of catalyst by a second metal. This approach was applied successfully for the conventional Pd-Fe [22], Pd-Au [23, 24], and Pd-Pt [25] HDC catalysts; promising results were reported for Pd-Ni systems [26, 27]. The second component not only helps to delay deactivation but can also interact with palladium to form new and more efficient catalytic sites.

By now few works have been devoted to the production of bimetallic catalysts by the LED method. Thus, in [10, 28] the LED method was used to produce bimetallic Au-Ni/ Al_2O_3 catalysts by the consecutive deposition of Au and Ni from monometallic targets on the support granules. The activity and stability of the LED catalysts in chlorobenzene hydrodechlorination [10] were found to depend on the order of metal deposition. More stable catalysts were produced by the first supporting of gold and then nickel; the reverse deposition order provided the higher initial activity of the bimetallic catalyst. However, in contrast to Au-Ni catalysts obtained by the reductive deposition of Au onto Ni [29], no significant synergistic effects caused by the coaction of two metals was detected in the temperature range from 50 to 300 °C for Au-Ni LED catalysts. A synergistic effect in chlorobenzene HDC has been found for Au-Ni LED catalysts only at relatively high reaction temperature (350 °C) when the particle or atom mobility increases, and the restructuring of the catalyst surface becomes possible [10].

In this study the laser electrodispersion of the $\text{Ni}_{77}\text{Pd}_{23}$ alloy was for the first time used for the deposition of bimetallic nanoparticles on the surface of Al_2O_3 granules. The efficiency of the produced catalyst and its monometallic counterparts was compared using gas-phase chlorobenzene HDC as a test reaction.

Experimental

Synthesis of the catalysts by LED

Bimetallic NiPd/ Al_2O_3 and reference monometallic Ni/ Al_2O_3 and Pd/ Al_2O_3 samples were produced by the LED technique. The physical principles of the LED method for controlled fabrication of monodisperse metallic nanoparticles are described in detail elsewhere [30]. The metal nanoparticles were deposited on $\gamma\text{-Al}_2\text{O}_3$ granules (0.4–1 mm grain size, $S_{\text{BET}} = 180 \text{ m}^2/\text{g}$, $V_{\text{pore}} = 0.55 \text{ cm}^3/\text{g}$, JSC “Katalizator”, Russia). A NiPd cast alloy comprising 77 at.% (65 wt.%) of Ni and 23 at.% (35 wt.%) of Pd or pure metals (Ni – 1u grade Ni alloy, Russian State Standard GOST 849-97, actual Ni content – 99.95 %; Pd – 99.9 grade Pd alloy, Russian State Standard GOST 13462-2010, actual Pd content – 99.95 %) were used as a source of metal nanoparticles to prepare bimetallic and monometallic catalysts, respectively. The metal loading was controlled by varying the deposition time according to the calibration curves [12]. Relatively uniform distribution of metal nanoparticles on the surface of alumina granules was achieved by their continuous stirring on a piezoceramic plate (total area of 3.14 cm^2) vibrating at the frequency of 16 kHz [12]. In each experiment 15 g of alumina were used. The catalysts were stored in air. To facilitate TEM investigation of the metal particles produced from the alloy target some control samples were prepared by LED method using TEM Cu grids as a support. In this case no stirring was applied. Additional details about the samples preparation by the LED method are provided in Supplementary Material, S1.

Sample characterization

Metal content in the catalysts was measured by the atomic absorption spectrometry (AAS) on a Thermo iCE 3000 spectrometer (Thermo Fisher Scientific Inc., USA). The catalyst (0.1 g) was treated with 10 ml of aqua regia ($\text{HCl}:\text{HNO}_3 = 4:1$) for 1 h. The solution was diluted with 90 ml of H_2O . The metal content in the solution was calculated from its atomic absorption using the calibration curve for standard solutions, the atomic absorption of which was determined in the same experiment. According to AAS data, the NiPd/ Al_2O_3 sample

comprises 0.0032 wt.% of Ni and 0.0018 wt.% of Pd. In monometallic reference samples, the content of metal (Ni or Pd) was 0.005 wt.%. The relative error in the metal content measurement was less than 1 %.

High-resolution transmission electron microscopy (HRTEM) investigation was carried out on a JEOL JEM 2100F/UHR (Jeol, Japan) microscope combined with a JED-2300 X-ray spectrometer for Energy Dispersive X-Ray analysis (EDS). To obtain a sample for analysis of alumina supported catalysts, the outer layer of granules was scraped off with a scalpel. Then scraped particles were ultrasonically dispersed in ethanol with the subsequent deposition of a drop of the suspension on a carbon-coated Cu TEM grid. Bright field (BF), annular dark field (ADF) and high-angle annular dark field (HAADF) modes were used for the TEM analysis of the composition and size distribution of metal particles. From 300 to 380 particles were processed to determine the particle size distribution. The elemental composition of nanoparticles was analyzed by EDS on the same TEM instrument operated in the STEM mode. The lattice d-spacing was calculated from the fast Fourier transformation (FFT) patterns of the planes visible in the high-resolution TEM image, using ImageJ software [31]. The assignment of the d-spacing to a certain reflection of crystalline particles was verified by the distance ratios and angles in the face-centered cubic (*fcc*) lattice.

XPS spectra were acquired on a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, UK) using a monochromatic Al K_{α} source ($h\nu = 1486.7$ eV, 150 W). The pass energy of the analyzer was 40 eV. The binding energy scale of the spectrometer was preliminarily calibrated using the position of the peaks for the Au 4f_{7/2} (83.96 eV) and Cu 2p_{3/2} (932.62 eV) core levels of pure metallic gold and copper. The Kratos charge neutralizer system was used and the spectra were charge-corrected to give Al 2p peak a binding energy of 74.2 eV. To study the reduction of the NiPd/Al₂O₃ catalyst, it was treated in situ in the high-pressure catalytic cell connected to the spectrometer vacuum chamber. For this purpose, the sample was placed in a quartz holder and heated in the cell in a flow of (5 % H₂ + 95 % Ar) gas mixture at 1 atm pressure up to a desired temperature with a heating rate of 5–10 °C/min. The following reduction temperatures and durations were used: 150 °C (20 min), 300 °C (30 min), and 450 °C (30 min). After reduction, the holder with the sample was cooled in the gas flow and transferred into the analytical chamber after pumping down the cell. The CasaXPS software was used for the background subtraction and fitting of the XPS spectra.

Catalytic tests

The catalytic properties of the samples were studied in HDC of chlorobenzene (Acros Organics, 95 %). The reaction was carried out in a flow type quartz reactor with a fixed catalyst bed using the procedure reported in [14]. In each catalytic test 50 mg of a catalyst was placed into the reactor and heated in H₂ flow (12 ml/min) up to a desired reaction temperature. Then the mixture of chlorobenzene vapor with hydrogen (molar ratio C₆H₅Cl: H₂ = 1:50) was passed through the reactor at a flow rate of 12 ml/min. Every 20 min, the reaction products were sampled from the reactor outlet and analyzed by GC on an Agilent 6890N chromatograph (30 m DBWax capillary column, flame ionization detector, the relative error in the peak area measurement was ±5 %). After achieving a constant conversion of chlorobenzene (deviations less than 1–2 %) at the fixed temperature, the reactant supply was terminated, and the temperature was raised to the next value in a flow of H₂. The catalytic efficiency of the samples was evaluated in the temperature range of 100–350 °C by comparing the chlorobenzene conversion at different reaction temperatures.

Results and discussion

TEM/EDS analysis of PdNi nanoparticles on TEM copper grid

An important question of this study was: what kind of metal particles are formed during LED of bimetallic (Ni₇₇Pd₂₃) and monometallic (Ni and Pd) targets? To confirm the possibility of bimetallic particles deposition,

Fig. 1: The bright-field (a), corresponding annular dark field (b) TEM images and the particle size distribution (c) of metal particles deposited by LED on a TEM Cu grid from the $\text{Ni}_{77}\text{Pd}_{23}$ alloy.

the sample specially prepared using a TEM copper grid as a support for NiPd particles was studied by TEM. The BF and corresponding ADF TEM images of this sample are shown in Fig. 1a and b. The dark areas in the BF TEM image that become bright in the ADF TEM image correspond to the metal-containing areas in the studied material. No large aggregates of metallic particles were found. The uniform distribution of fine metal nanoparticles is clearly seen in the presented images and from the narrow and unimodal particle size distribution histogram, depicted in Fig. 1c. The observed mean particle size is 1.0 nm, which is approximately twice smaller than the size of Ni and Pd particles formed by LED from the monometallic target [10]. The dispersion of particles was estimated from TEM data as an inverse value of the volume/surface mean diameter (d_{vs}) that is sensitive to the variation of small particle sizes. The dispersion was found to be 0.84 for $\text{PdNi}/\text{Al}_2\text{O}_3$, 0.41 for $\text{Pd}/\text{Al}_2\text{O}_3$, and 0.59 for $\text{Ni}/\text{Al}_2\text{O}_3$.

The elemental composition of supported metal nanoparticles was studied by the EDS spectroscopy in the STEM mode. As the thickness of the sample was small (since it is determined by the diameter of the deposited metal particles) X-ray absorption and secondary fluorescence were minimized during EDS microanalysis. Therefore, the accuracy of the EDS analysis and the spatial resolution for the selected areas of such thin samples are higher than those for thick samples. All the EDS spectra comprise Ni $K\alpha$ (7.47 keV) and Pd $L\alpha$ (2.83 keV) lines. They were acquired from one rectangular area of $17 \times 13 \text{ nm}^2$ and nine arbitrarily chosen points. The analyzed areas and the corresponded relative elemental compositions are presented in Fig. 2 and Table 1.

According to EDS, all the analyzed areas contain both Pd and Ni, which testifies the formation of bimetallic particles during LED deposition from the bimetallic PdNi target. Though the possibility of the presence of monometallic particles cannot be completely excluded, the EDS data demonstrate the predominance of bimetallic PdNi particles in the produced sample. The Ni/Pd ratio is significantly different in different analyzed spots, with the Ni atomic content being always higher than that of Pd. The calculated mean value of the Ni/Pd atomic ratio (Table 1) is 1.7 (1.5 for the rectangular area containing more than 100 particles) that is

Fig. 2: ADF-STEM images of metal particles deposited by LED on a TEM Cu grid from the $\text{Ni}_{77}\text{Pd}_{23}$ alloy. The location of the areas analyzed by EDS are indicated by yellow square and dots.

Table 1: The relative Pd and Ni content and their ratio in NiPd/(Cu grid) determined by EDS.

	Analyzed area										Mean value ^b
	1 ^a	2	3	4	5	6	7	8	9	10	
Ni, at. %	60	57	61	63	73	68	62	56	52	74	62.9
Pd, at. %	40	43	39	37	27	32	38	44	48	26	37.1
Ni/Pd	1.5	1.3	1.6	1.7	2.7	2.1	1.6	1.3	1.1	2.8	1.7

^aRectangular area of $17 \times 13 \text{ nm}^2$.

^bCalculated for areas 2–10.

significantly lower than that in the PdNi target alloy ($\text{Ni/Pd} = 3.3$). The enrichment of bimetallic PdNi particles with Pd is a well-established fact [32, 33] but more typical for larger particles. In addition, the depth of EDS analysis is higher than the average metal particle size providing no possibility to compare the surface and bulk composition of produced bimetallic particles.

The difference in the Ni/Pd molar ratio between the deposited particles and the target alloy can result from the nonuniform distribution of metals in the bimetallic target and its melted surface layer and from the partial segregation of metals during cascade fission of melted drops. The areas analyzed by TEM/EDS are very small, less than 1 nm^2 , and therefore these results may not be representative for the bulk composition of the sample. As it will be demonstrated below, the bulk AAS elemental analysis of the sample reveals higher Ni/Pd ratio which is close to that in the target alloy.

One of the nanoparticles observed in the high-resolution TEM image (Fig. 3a) was chosen for the more detailed analysis, which reveals its crystalline structure (Fig. 3b). The simulated electron diffraction pattern of this nanoparticle allows calculating the interplanar spacings d_1 and d_2 (Fig. 3c). They were found to be 1.8 and 1.3 Å, respectively. Their ratio of 1.38 and the angle between the corresponding planes of 44° may be attributed to (200) and (220) planes of a face-centered cubic lattice (for the perfect *fcc* lattice the $d(200)/d(220)$ ratio is equal to 1.41 and the angle between planes is 45°).

The calculated interplanar spacings for analyzed particle are between those for pure palladium and nickel, which confirms NiPd alloying. The composition of the alloy may be calculated using the Vegard's law:

$$a(\text{NiPd}) = (1 - x) \times a(\text{Ni}) + x \times a(\text{Pd}),$$

where $a(\text{NiPd})$ is the calculated lattice constant of the alloy equal to 3.68 Å, $a(\text{Ni})$ is the Ni lattice constant equal to 3.52 Å, $a(\text{Pd})$ is the Pd lattice constant equal to 3.88 Å, and x is the Pd mole fraction in the alloy.

Fig. 3: HRTEM image of NiPd nanoparticles deposited on a Cu-grid (a); (b) 3-fold magnification of the image of the particle designated by a circle; (c) simulated electron diffraction pattern of the selected particle.

According to these calculations, the relative Ni and Pd contents in bimetallic particle are 60 and 40 at.%, respectively. The calculated Ni/Pd molar ratio is within the range found by EDS analysis.

The Ni-Pd binary system is known to form a continuous solid solution with a minimum in the liquidus [34]. In the LED method the surface layer of the initial bimetallic target is melted under the impact of high-power pulsed laser beam followed by the formation of laser torch plasma. The temperature of laser torch plasma reaches about 10 eV (approx. $1.16 \cdot 10^5$ K), so the initial drops coming to the laser plasma are charged negatively. Charged clusters tend to fission forming two charged fragments. This process continues until the surface tension force is compensated by the Coulomb repulsive one [30]. As a result of such cascade fission process the plenty of nanosized metal particles are formed. When NiPd alloy target is used as a metal source, the liquid drops knocked out from the NiPd alloy target by laser impulse are very likely to contain both metals. This is confirmed by TEM/EDS results that testify the absence of monometallic particles in the material deposited from the NiPd alloy.

The size of metal particles produced by LED mainly depends on the electron work function of the material [30]. The difference in the work function of the alloy and pure metals may be a reason for the different dispersion of supported particles obtained from pure metals and alloy; this difference also influences the composition of nanoparticles, produced from the alloy of two metals. The work function is determined by the nature of atoms on the surface of particle, which in turn depends on the energy of the surface. Strong influence of the disordered and stressed surface area of bimetallic nanoparticles may cause alloy segregation. To decrease the surface energy the most mobile element (Pd) will localize on the surface. The experimentally measured surface energy is 2.380 J/m² for Ni and 2.00 J/m² for Pd [35], so the surface of NiPd alloy should be slightly enriched with palladium. This is consistent with the increased Pd content in LED-produced nanoparticles according to TEM-EDS compared to the composition of the NiPd target. But the energy of intermetallic Pd-Pd, Ni-Ni and Pd-Ni bonds should affect the distribution of metals in the particle. Considering the presence of both metals on the surface of melted drops produced by LED, the final size of bimetallic particles is expected to be quite different from that of monometallic particles produced from pure Pd or Ni target.

As the results presented in this section show, it is the bimetallic particles that are formed by LED method when bimetallic palladium-nickel target is used as a metal source.

STEM/EDS analysis of NiPd nanoparticles deposited by LED on alumina

The STEM–EDS mappings of NiPd/ Al_2O_3 sample deposited by LED from NiPd alloy on alumina support are presented in Fig. 4. In contrast to NiPd nanoparticles deposited directly on the flat TEM grid, in this sample Pd and Ni are not uniformly distributed over the support. For example, aluminum is clearly seen in the upper part of its mapping whereas palladium and nickel are almost absent in these areas. Probably these areas correspond to the bulk of the initial alumina granules, where metal nanoparticles are not deposited by the LED technique. At the same time Pd and Ni show very similar mappings. Besides, only a small fraction of metal particles is distinctly visible on the Al_2O_3 surface. Due to their high contrast they can be attributed rather to Pd. Such a small number of visible metal particles in comparison with the Cu-grid supported sample can be explained by the oxidized state of the fraction of deposited metals (more probably, Ni) due to the chemical interaction with alumina or as a result of storage in air. The interaction of Ni with alumina during catalysts preparation is well known to result in the formation of both Ni oxide and aluminates [36]. These compounds are poorly visible in TEM images due to their low contrast with respect to alumina, especially when they are formed as a surface non-stoichiometric film. Therefore, it is impossible to accurately estimate the size of metal particles in alumina-supported sample from STEM data. It can only be affirmed that it does not exceed 4–5 nm (Fig. 4a).

The TEM images of PdNi/ Al_2O_3 and the STEM-EDS results for some selected areas of this sample are presented in Fig. 5 and Table 2. Similar to EDS mappings, some area attributed to the bulk of the initial catalyst granules do not contain Ni and Pd (Table 2). Simultaneous presence of both metals was found by EDS in

Fig. 4: Bright field STEM image (a) and EDS element mappings (b–d) of NiPd/ Al_2O_3 .

Fig. 5: The HR TEM (a) and HAADF/STEM (b) images of NiPd/Al₂O₃ and the EDS spectra from the selected areas of HAADF/STEM image (c).

Table 2: The relative Pd and Ni content and their ratio in NiPd/Al₂O₃ determined by EDS.

	Analyzed area							
	1–7	8	9	10	11–20	21	22	23
Ni, at. %	–	68	65	64	–	75	73	74
Pd, at. %	–	32	35	36	–	25	27	26
Ni/Pd	–	2.1	1.9	1.8	–	3.0	2.7	2.9

three areas (Fig. 5b,c) and in six spots (from total 23) (Table 2). No areas were found in which only one of the deposited metals was detected. The mean Ni/Pd molar ratio calculated from EDS data is 2.8. This value is higher than that obtained for the NiPd sample deposited on a Cu grid, and closer to the Ni/Pd ratio in the target alloy (3.3). As it was mentioned above, the spatial resolution of EDS microanalysis depends on the thickness of the sample. Since the analyzed sample in the case of NiPd/Al₂O₃ is thicker than that in the case

of NiPd/(Cu-grid), the EDS spectra obtained at the same conditions correspond to the larger analyzed area of NiPd/Al₂O₃. Therefore, the results of EDS analysis of NiPd/Al₂O₃ reflect the average composition of larger amount of material, which is close to the composition of the initial alloy. The Ni/Pd molar ratio found by AAS after complete dissolution of this sample is 3.2, which practically coincides with the composition of the initial target alloy.

Summarizing the results obtained by TEM and AAS, it can be assumed that the LED deposition from the NiPd alloy on a Cu grid provides uniformly distributed small bimetallic particles, the composition of which slightly varies from particle to particle. Deposition on spherical alumina granules leads to the homogeneous distribution of both metals only on the outer surface of granules, so the sample for TEM analysis contained the surface areas of the initial granules comprising both metals and the areas from the bulk of the granules with no metal loading. A small number of visible metal particles in TEM images and a weak contrast of metal-containing areas relative to alumina suggest a partial oxidation of metals in contact with the alumina support. Earlier such oxidation of Ni supported by LED on alumina was observed in [15].

XPS analysis

To reveal the oxidation state of the deposited metals in NiPd/Al₂O₃, as-prepared and stored in air for 6 months catalysts were investigated by XPS. The changes in the oxidation state of metals under in situ hydrogen treatment were also studied.

The relative content of elements in as-prepared NiPd/Al₂O₃ is shown in Table 3. The XPS Ni/Pd ratio is much higher than that found by EDS. Since palladium is predominantly observed in the metal state whereas nickel – in the oxidized form, the discrepancy in the composition obtained by EDS and XPS can be explained by the difference in the photoelectron escape depth which is larger for oxides than for metals.

The Ni2p XPS spectra of as-prepared, stored in air and in situ hydrogen reduced NiPd/Al₂O₃ are presented in Fig. 6. These spectra were fitted by Ni²⁺ and Ni⁰ components (Table 4).

The Ni2p XPS spectra for all NiPd/Al₂O₃ samples are very similar. The intense shake-up satellites in the spectra confirm the presence of the Ni²⁺ oxidation state. But the line shape and the position of the Ni2p_{3/2} peak (856.0–856.5 eV) are different from those of NiO (854.5–854.8 eV) [37]. At the same time the observed spectra are close to that of nickel aluminate (856.2–856.3 eV) [38] and Ni(OH)₂ (856.1–856.2 eV) or other oxidized Ni species (856.5 eV) resulted from the interaction of Ni(OH)₂ with palladium [39]. The separation between the main and satellite peaks in the spectra is about 6 eV, which agrees with that of nickel aluminate. According to [40] the separation of 6.3 ± 0.3 eV is typical for Ni bonding in aluminate, whereas for nickel in NiO it equals to 7.1 ± 0.1 eV.

Nickel in all samples is predominantly in the oxidized Ni²⁺ form, most likely in the aluminate surface phase. A small amount (3 %) of Ni⁰ (Ni2p_{3/2} binding energy of 852.6 eV) was detected only in the as-prepared NiPd/Al₂O₃ sample. The fitting of the Ni2p XPS spectra yielded less than 1 % of Ni⁰ after hydrogen treatment of NiPd/Al₂O₃ at 150, 300 and 450 °C, which is below the detection limit. Therefore, oxidized Ni in NiPd/Al₂O₃ is very resistant to reduction. Such stability is typical for nickel-alumina spinel that usually starts to reduce only at 600 °C [41]. In contrast, NiO reduction temperature is in the range of 300–450 °C depending on the particle size and their distribution in the bulk and on the surface of a support.

As-prepared monometallic Ni/Al₂O₃ LED sample also comprises almost 100 % of nickel in the Ni²⁺ oxidation state. But its Ni2p XPS spectrum differs from those of as-prepared and air-stored NiPd/Al₂O₃ [6]. It

Table 3: Surface XPS composition and Ni/Pd ratio in NiPd/Al₂O₃.

Ni	O	Pd	C	Concentration, at. %		Ni/Pd ratio
				Cl	Al	
11.4	48.8	1.5	19.3	0.2	18.8	7.6

Fig. 6: Ni 2p XPS spectra of as-prepared (1), stored in air (2) and reduced at 150 °C (3), 300 °C (4) and 450 °C (5) NiPd/Al₂O₃.

Table 4: Fraction of nickel and palladium in different species determined by XPS in the as-prepared, stored in air and hydrogen reduced NiPd/Al₂O₃.

Treatment conditions	Exposure time	Fraction of Ni (Pd) species, % (Binding energy of Ni2p _{3/2} (Pd3d _{5/2}) XPS line, eV)				
		Ni ⁰ (852.5)	Ni ²⁺ (~856.0)	Pd ⁰ (335.3)	Pd ²⁺ (336.6)	Pd ⁿ⁺ (338.0)
– (as prepared)	–	6	94	72	18	10
Air, 25 °C	6 months	0	100	14	51	35
5%H ₂ + 95%Ar, 150 °C	30 min	<1	100	32	43	25
5%H ₂ + 95%Ar, 300 °C	30 min	<1	100	68	22	10
5%H ₂ + 95%Ar, 450 °C	30 min	<1	100	85	10	5

contains a broad main peak with a shoulder at the lower binding energy side. This spectrum may be fitted by two components characteristic for NiO (854.3 eV) and nickel aluminate (855.9 eV). Note that in the bimetallic sample the Ni2p_{3/2} peak of Ni²⁺ species is observed at higher binding energy (856.0–856.5 eV) probably due to the formation of nickel aluminate or other Ni²⁺ species on the Ni-Pd interface.

The reduction ability of mono- and bimetallic NiPd systems strongly differs. While hydrogen treatment at 150 °C does not change the Ni²⁺ oxidation state both in NiPd/Al₂O₃ and Ni/Al₂O₃, the reduction at 350 °C led to a new peak in the Ni2p XPS spectrum of monometallic sample characteristic for metallic nickel [6]. After treatment at 450 °C up to 50 at.% of Ni²⁺ was reduced to Ni⁰. So Ni²⁺ in monometallic catalyst can be reduced much easily, possibly due to the presence of surface NiO which is much more prone to the reduction than nickel-alumina spinel predominated in the bimetallic sample.

The Pd3d XPS spectra of as-prepared, stored in air, and hydrogen reduced NiPd/Al₂O₃ are presented in Fig. 7. To reveal the contribution of oxidized (Pdⁿ⁺ and Pd²⁺) and zero-valent (Pd⁰) species, the spectra were fitted by three components. The asymmetric component at the binding energy of 335.5 eV corresponds to Pd⁰, whereas the symmetric component at the binding energy of 336.6 eV can be attributed to Pd²⁺ in PdO, and

Fig. 7: Pd 3d XPS spectra of as-prepared (1), stored in air (2) and reduced at 150 °C (3), 300 °C (4) and 450 °C (5) NiPd/Al₂O₃.

the component with the binding energy of 338.0 eV to Pdⁿ⁺ in palladium aluminate [42]. The relative contents of Pd⁰, Pd²⁺ and Pdⁿ⁺ are presented in Table 4. The as-prepared NiPd/Al₂O₃ sample contains a large fraction of metallic palladium (72 %), which decreases to 14 % after prolonged storage in air. Hydrogen treatment at 150 °C results only in partial reduction of oxidized Pd. The increase of treatment temperature leads to a significant reduction of Pd (up to 85 % at 450 °C) (Table 4). Moreover, even after high temperature reduction the Pd3d lines of NiPd/Al₂O₃ remain broader than they are observed in metal Pd, which indicates incomplete Pd reduction. Note that the similar treatment of monometallic Pd/Al₂O₃ LED sample at 150 °C leads to a nearly complete reduction of Pd²⁺ to Pd⁰ (See Supplementary Material, S2, Fig. S2).

Thus, according to XPS data not only Ni, but also Pd in NiPd/Al₂O₃ is less reducible in comparison with monometallic counterpart probably because of the interaction with the alumina surface. The deposition of bimetallic nanoparticles from NiPd alloy target on alumina results in the formation of nickel aluminate species completely resistant to hydrogen reduction up to 450 °C, while deposition from Ni target provides the formation of not only spinel, but also NiO that can be reduced much easier. The major part of palladium in as-prepared NiPd/Al₂O₃ is in metal state, but it is very prone to oxidation during storage in air. Only a small part of palladium participates in the formation of aluminate under the interaction with the alumina support.

The decomposition and oxidation of bimetallic particles during their deposition on alumina are caused by the strong interaction of highly dispersed metal particles with the support. It is possible to assume that Pd nanoparticles in as-prepared NiPd/Al₂O₃ are located on the surface of Al₂O₃ and decorated by the thin layer of nickel aluminate. Usually, the coexistence of Pd and Ni oxides on alumina facilitates Ni reduction lowering the reduction temperature by 30–150 °C [43]. The stability of Ni²⁺ to hydrogen reduction confirms the strong interaction of nickel with alumina in the case of bimetallic sample. The possible encapsulation of PdO with compounds comprising Ni²⁺ species in NiPd/Al₂O₃ may hinder Pd²⁺ species reduction in contrast to monometallic Pd/Al₂O₃. It should be noted that the LED deposition provides nearly atomically homogeneous distribution of nickel and palladium as well as their close contact with each other and the surface of alumina. A large number of these contacts enhances the role of interactions between all components of catalytic systems resulting in new properties of LED material.

Catalytic properties in chlorobenzene hydrodechlorination (HDC)

The as-prepared NiPd/Al₂O₃ sample was tested as a catalyst in the vapor-phase continuous-flow chlorobenzene HDC and compared with its monometallic counterparts. Despite the extremely low metal content (0.005 wt.%) in the catalysts, they were active in HDC reaction. No metal loss was observed during catalytic test. The temperature dependencies of the steady-state conversion are shown in Fig. 8a. Ni/Al₂O₃ demonstrated the lowest catalytic activity in the whole temperature range. Benzene was the only organic product in the presence of this catalyst. Both Pd-containing catalysts showed similar catalytic activity, while benzene and cyclohexane were detected as organic reaction products. The steady-state values of selectivity for Pd/Al₂O₃ and NiPd/Al₂O₃ depended on the reaction temperature. The selectivity of cyclohexane formation at 50 and 100 °C, that is at low chlorobenzene conversion, was about 80 and 50 %, correspondingly. Starting from 150 °C the cyclohexane selectivity significantly dropped to about 6 % at 150 °C and then decreases to 1 % at 200–350 °C.

The examples of the conversion vs time-on-stream plot for the reaction temperature of 200 °C for as-prepared NiPd/Al₂O₃ and its monometallic (Ni/Al₂O₃ and Pd/Al₂O₃) counterparts, contained 0.005 wt.% of metal, are depicted in Fig. 8b. Ni/Al₂O₃ shows fast deactivation (chlorobenzene conversion drops from 45 to 10 % within 130 min). Earlier the low stability of Ni/Al₂O₃ prepared by LED method with various Ni loading (from 0.0002 to 0.03 wt.%) was demonstrated in [10, 14]. In our work for Ni/Al₂O₃ last three points in the plots, for which the chlorobenzene conversion is stable within ±5 %, were used to calculate the average steady-state conversions that are plotted vs temperature in Fig. 8a.

Much higher stability demonstrated Pd/Al₂O₃, on which conversion decreases from 85 to 70 % within 220 min. The bimetallic catalyst is the most stable one as the decrease of chlorobenzene conversion is less than 5 % after 175 min time-on-stream.

Monometallic Ni/Al₂O₃ shows the least catalytic activity in whole temperature range. As it was mentioned above, initial chlorobenzene conversion for Ni/Al₂O₃ is relatively high but this catalyst rapidly deactivates under reaction condition before reaching the steady-state conversion values. Pd-containing catalysts are more active at temperatures higher 150 °C. For both Pd-containing catalysts the steady-state conversion of chlorobenzene increases from 40 to 50 % at 150 °C to more than 90 % at higher reaction temperatures due to the acceleration of the reaction according to the Arrhenius equation. In addition, as it was found by in situ TPR in the catalytic cell of the XPS spectrometer, Pd²⁺ (18 % in as-prepared sample, according to XPS) starts to reduce at temperatures higher than 150 °C. The reduction of Pd²⁺ to Pd⁰ leads to the increase in the number of catalytically active sites.

Fig. 8: The temperature dependence of the steady-state chlorobenzene conversion over NiPd/Al₂O₃, Pd/Al₂O₃ and Ni/Al₂O₃ (a) and the chlorobenzene conversion at 200 °C versus the reaction time over mono- and bimetallic LED catalyst with the total metal content of 0.005 wt.% (b).

At temperatures higher than 150 °C the chlorobenzene conversions on NiPd/Al₂O₃ and Pd/Al₂O₃ are higher than that on Ni/Al₂O₃. At the same time, at 150 and 200 °C NiPd/Al₂O₃ shows even higher conversion compared to Pd/Al₂O₃, though the difference is not so big: only 9 % at 150 °C and 16 % at 200 °C. The obvious similarity between these systems can be caused by the fact that in both catalysts the active component is palladium. Indeed, XPS data demonstrate that only oxidized Ni that shows no activity in HDC exists in bimetallic catalyst. Moreover, Ni²⁺ species found in this catalyst are very resistant to reduction up to 400 °C that is higher than the reaction temperatures used in this work. Apparently, the activation of chlorobenzene and hydrogen proceeds on metal palladium.

TOF values calculated on the base of chlorobenzene conversion at 150 °C using the total metal loading in the monometallic catalysts were found to be $3.3 \times 10^6 \text{ h}^{-1}$ for Ni/Al₂O₃ and $3.0 \times 10^7 \text{ h}^{-1}$ for Pd/Al₂O₃. Taking into account only the surface fraction of the active metal could result in even greater TOF values. Very high TOF values due to very low metal loadings are the unique feature of LED catalysts [10].

The calculation of true TOF value for bimetallic catalyst is difficult, considering mostly separate location of Pd and Ni in bimetallic LED sample, predominantly oxidized state of Ni and ambiguity in the determination of the particle size. The estimation on the base of the total content of both metals gives the value of $2.8 \times 10^7 \text{ h}^{-1}$ at 150 °C (see Supplementary Material, S3, Table S1), that is much higher than for Ni/Al₂O₃, but slightly less than for Pd/Al₂O₃. However, if only Pd is the active component of bimetallic catalyst, and the oxidized nickel in the sample plays a different role, the TOF value has to be calculated on the base of Pd loading, and in this case this TOF value ($5.7 \times 10^7 \text{ h}^{-1}$) is higher than for monometallic Pd/Al₂O₃ catalyst, in which Pd content is higher.

To compare LED systems with the catalysts, prepared by common ‘wet’ methods, we calculated TOF value at 150 °C for 6 % Ni/Al₂O₃ catalyst prepared by wet impregnation and tested in similar conditions [44]; it was only 14.4 h^{-1} (see Table S1). The comparison of the temperature dependences of chlorobenzene conversion on this catalyst and on LED-prepared samples, described in this work, at the same reaction conditions is shown in Supplementary Information, S3, Fig. S3.

So, bimetallic NiPd/Al₂O₃ outperforms the comparative monometallic Pd/Al₂O₃ in chlorobenzene conversion at 150–200 °C and in stability despite the lower Pd content (0.0018 and 0.005 wt.% Pd, respectively) and higher resistivity of Pd to the reduction with H₂. A possible reason for this difference is the formation of new active sites on the interface between palladium and nickel aluminate. The presence of nickel can also ensure higher dispersion of Pd and its more uniform distribution over the surface of a support. The uniform distribution of metals at the atomic level provides the high concentration of active sites and the effective use of catalytically active metals.

The chlorination of metal by hydrogen chloride is usually considered as the main reason for HDC catalysts deactivation [18]. The high operation stability of NiPd/Al₂O₃ observed in our study is probably attributed to the protective properties of nickel-alumina spinel. In bimetallic catalysts HCl can react with the surface of nickel aluminate phase, thus preserving the Pd⁰ sites required for catalysis. Nickel aluminate is much more stable to the action of HCl in comparison with NiO [45]. The improvement in the stability of Ni/Al₂O₃ catalyst due to nickel aluminate formation that prevents strong interaction between HCl and metallic nickel was mentioned in [46] for 1,1,2-trichloroethane hydrodechlorination.

The TEM, XPS, and catalytic test results presented in this work allow suggesting the mechanism of catalyst formation during LED deposition from NiPd alloy. The laser beam knocks out large bimetallic drops from the surface of the target. Under their cascade fission tiny melted droplets of PdNi alloy are formed. The composition, that is the Ni:Pd ratio, is most probably slightly different for different droplets due to phase instability that grows in the nano-range, and due to the temperature effects. In case of NiPd nanoparticles supported by LED on a TEM Cu grid no significant oxidation of alloy components is expected. In contrast, during LED deposition on the surface of Al₂O₃ a significant part of NiPd nanoparticles decomposes due to the almost complete and rapid oxidation of nickel in contact with alumina, which results in the formation of Ni²⁺ species. The higher dispersion of Ni in bimetallic nanoparticles in comparison with monometallic ones provides predominant nickel aluminate formation confirmed by XPS. Due to the difference in the composition of bimetallic particles observed in PdNi/Cu-grid the Pd particle size distribution in bimetallic catalyst

may be wider than in its monometallic counterpart. When Ni is extracted from bimetallic particles due to the interaction with support, smaller or bigger Pd particles are formed, depending on the initial Ni:Pd ratio in each droplet. Tiny Pd particles are easily oxidized [47] so the total amount of Pd^{2+} and Pd^{n+} in as-prepared $\text{NiPd}/\text{Al}_2\text{O}_3$ is 28 % (Table 4).

The atomic restructuring of bimetallic particles was earlier observed in [17]. Under LED on Al_2O_3 it leads to the formation of bifunctional active sites consisted of neighboring Pd^0 and Ni^{2+} species. Ni^{2+} species readily form NiCl_2 by the interaction with Cl atoms adsorbed on the catalyst surface after destruction of Cl–C bond during HDC on Pd^0 sites located in the close vicinity. Pd^0 is also responsible for the activation of molecular hydrogen required for the substitution of Cl in the adsorbed chlorobenzene molecule. Activation of hydrogen on Pd^0 sites is usually accompanied by the spillover of activated hydrogen species on a support. For the alumina-supported metals, hydrogen atoms formed on the metal particles by the dissociative adsorption of H_2 can spillover onto alumina through the action of surface hydroxyl groups [48]. The efficiency of hydrogen spillover process enhances on the nanosized Pd particles with high surface energy [49]. Besides, the presence of new active sites at the interface between Pd and Ni-containing oxide species in $\text{NiPd}/\text{Al}_2\text{O}_3$ provides more favorable conditions for the adsorption and activation of reactants. Such processes are under active study in the heterogeneous catalysis [1, 4, 50]. In contrast, when only Ni droplets are colliding with alumina surface, NiAlO_x layer formed between the droplet and alumina softens their interaction. As a result NiO is formed in the significant amount in addition to nickel aluminate. NiO can be easily reduced to form Ni^0 that is active in hydrodechlorination. But its chlorination in contact with HCl by-product cause the encapsulation of the active particles with NiCl_2 and fast deactivation [14].

Conclusions

The formation of bimetallic particles produced by laser electrodispersion of the $\text{Ni}_{77}\text{Pd}_{23}$ alloy target was found to be affected by the support nature. On a TEM Cu grid support the uniform distribution of about 1 nm bimetallic size-selected PdNi particles was observed. But the Ni/Pd ratio is different for different particles and its mean value is lower than that in the target alloy. This may result from the Pd enrichment of the surface of bimetallic target melted by a laser beam or from the inhomogeneity of the bimetallic target.

In contrast, when alumina granules are used as a support the decomposition of alloy particles takes place. The main reason for the bimetallic particles decomposition is their high dispersion and strong interaction with alumina. The Ni/Pd molar ratio in $\text{NiPd}/\text{Al}_2\text{O}_3$ measured by AAS is close to that in the target alloy. According to EDS, both metals are located in the same areas. Most likely, uniformly distributed on the alumina surface Pd particles are decorated by the thin film of nickel aluminate. Highly dispersed Ni-containing species in $\text{NiPd}/\text{Al}_2\text{O}_3$ are not reduced by H_2 even at 450 °C, as it was shown by in situ TPR experiments in the catalytic cell of the XPS spectrometer. Possibly because of their small size Pd particles are easily oxidized during storage in air. Not only Ni, but also Pd in $\text{NiPd}/\text{Al}_2\text{O}_3$ are much more resistant to reduction than in the similar monometallic catalysts. Reference $\text{Pd}/\text{Al}_2\text{O}_3$ sample with somewhat higher metals loading (0.005 wt.% in $\text{Pd}/\text{Al}_2\text{O}_3$ against 0.0018 wt.% Pd in bimetallic catalyst) contains larger nanoparticles with the size of about 2 nm.

Intrinsic core-shell structure of $\text{PdNi}/\text{Al}_2\text{O}_3$ LED catalyst provides high accessibility of deposited metals for reagent adsorption and activation during continuous-flow vapor-phase HDC of chlorobenzene by H_2 . As a result, $\text{NiPd}/\text{Al}_2\text{O}_3$ catalyst with very low metal-loading (0.005 %) shows high chlorobenzene conversion to benzene (87 % at 200 °C), much higher than that on a similar monometallic $\text{Ni}/\text{Al}_2\text{O}_3$ and even $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts with a twice higher Pd loading. The probable reasons for the high chlorobenzene conversion on $\text{NiPd}/\text{Al}_2\text{O}_3$ catalyst are the formation of new active sites on the interface between palladium and nickel aluminate and the difference in the dispersion of palladium in nanoparticles. The stability of $\text{NiPd}/\text{Al}_2\text{O}_3$ is also much better than that of its monometallic counterparts. Such enhancement can be explained by the protective action of nickel-containing compounds that interact with the adsorbed chlorine species formed

during dissociative chemisorption of chlorobenzene. This interaction prevents chlorination of Pd⁰ that is unfavorable for the H₂ activation.

Highlights

- Bimetallic NiPd nanoparticles were produced by laser electrodispersion of the Ni₇₇Pd₂₃ alloy.
- The mean size of NiPd particles supported on TEM Cu-grid is about 1 nm.
- Core-shell NiPd/Al₂O₃ nanocomposite was synthesized.
- NiPd/Al₂O₃ shows high efficiency in chlorobenzene hydrodechlorination.
- New active sites on the interface of palladium/nickel aluminate are formed.

Acknowledgments: The authors acknowledge support from Lomonosov Moscow State University Program of Development for providing access to the XPS and TEM facilities.

Funding: This work was financially supported by RFBR, Funder Id: 10.13039/501100002261 (grant 16-03-00073) and in part by Institute of Metal Physics in the frame of “Magnit” Program.

References

- [1] O. G. Ellert, M. V. Tsodikov, S. A. Nikolaev, V. M. Novotortsev. *Russ. Chem. Rev.* **83**, 718 (2014).
- [2] V. Ponc. *Appl. Catal. A Gen.* **222**, 31 (2001).
- [3] V. Dal Santo, A. Gallo, A. Naldoni, M. Guidotti, R. Psaro. *Catal. Today* **197**, 190 (2012).
- [4] B. R. Cuenya. *Thin Solid Films* **518**, 3127 (2010).
- [5] T. N. Rostovshchikova, S. A. Nikolaev, E. S. Lokteva, S. A. Gurevich, V. M. Kozhevin, D. A. Yavsin, A. V. Ankudinov. in *Studies in Surface Science and Catalysis*, E. M. Gaigneaux, M. Devillers, S. Hermans, P. A. Jacobs, J. A. Martens, P. Ruiz (Eds.), pp. 263–266, Elsevier, Amsterdam, The Netherlands (2010).
- [6] E. V. Golubina, E. S. Lokteva, K. I. Maslakov, T. N. Rostovshchikova, M. I. Shilina, S. A. Gurevich, V. M. Kozhevin, D. A. Yavsin. *Nanotechnologies in Russia* **12**, 19 (2017).
- [7] G. Sharma, A. Kumar, S. Sharma, M. Naushad, R. Prakash Dwivedi, Z. A. Alotman, G. T. Mola. *Journal of King Saud University – Science* (2017), <http://dx.doi.org/10.1016/j.jksus.2017.06.012>.
- [8] J. Zhang, M. Chaker, D. Ma. *J. Colloid Interface Sci.* **489**, 138 (2017).
- [9] A. De Bonis, R. D’Orsi, M. Funicello, P. Lupattelli, A. Santagata, R. Teghil, L. Chiummiento. *Catal. Commun.* **100**, 164 (2017).
- [10] E. S. Lokteva, A. A. Peristyy, N. E. Kavalerskaya, E. V. Golubina, L. V. Yashina, T. N. Rostovshchikova, S. A. Gurevich, V. M. Kozhevin, D. A. Yavsin, V. V. Lunin. *Pure Appl. Chem.* **84**, 495 (2012).
- [11] V. M. Kozhevin, D. A. Yavsin, I. P. Smirnova, M. M. Kulagina, S. A. Gurevich. *Phys. Solid State* **45**, 1993 (2003).
- [12] E. S. Lokteva, T. N. Rostovshchikova, S. A. Kachevskii, E. V. Golubina, V. V. Smirnov, A. Y. Stakheev, N. S. Telegina, S. A. Gurevich, V. M. Kozhevin, D. A. Yavsin. *Kinet. Catal.* **49**, 748 (2008).
- [13] S. M. Nevskaya, S. A. Nikolaev, Y. G. Noskov, T. N. Rostovshchikova, V. V. Smirnov, S. A. Gurevich, M. A. Zabelin, V. M. Kozhevin, P. A. Tret’yakov, D. A. Yavsin, A. Y. Vasil’kov. *Kinet. Catal.* **47**, 638 (2006).
- [14] N. E. Kavalerskaya, E. S. Lokteva, T. N. Rostovshchikova, E. V. Golubina, K. I. Maslakov. *Kinet. Catal.* **54**, 597 (2013).
- [15] T. N. Rostovshchikova, V. V. Smirnov, S. A. Gurevich, V. M. Kozhevin, D. A. Yavsin, S. M. Nevskaya, S. A. Nikolaev, E. S. Lokteva. *Catal. Today* **105**, 344 (2005).
- [16] T. N. Rostovshchikova, V. V. Smirnov, V. M. Kozhevin, D. A. Yavsin, M. A. Zabelin, I. N. Yassievich, S. A. Gurevich. *Appl. Catal. A Gen.* **296**, 70 (2005).
- [17] R. M. Palomino, R. Hamlyn, Z. Liu, D. C. Grinter, I. Waluyo, J. A. Rodriguez, S. D. Senanayake. *J. Electron Spectros. Relat. Phenomena* **221**, 28 (2017).
- [18] E. Lokteva, E. Golubina, V. Likholobov, V. Lunin. in *Chemistry Beyond Chlorine*, P. Tundo, L.-N. He, E. Lokteva, C. Mota (Eds.), pp. 559–584, Springer International Publishing, Cham (2016).
- [19] M. A. Keane. *J. Chem. Technol. Biotechnol.* **80**, 1211 (2005).
- [20] M. A. Keane. *ChemCatChem* **3**, 800 (2011).
- [21] C. Amorim, G. Yuan, P. M. Patterson, M. A. Keane. *J. Catal.* **234**, 268 (2005).
- [22] H. Y. Zhou, X. H. Xu, D. H. Wang. *J. Environ. Sci.* **15**, 647 (2003).

- [23] M. S. Wong, P. J. J. Alvarez, Y.-l. Fang, N. Akçin, M. O. Nutt, J. T. Miller, K. N. Heck. *J. Chem. Technol. Biotechnol.* **84**, 158 (2009).
- [24] J. C. Velázquez, S. Leekumjorn, Q. X. Nguyen, Y.-L. Fang, K. N. Heck, G. D. Hopkins, M. Reinhard, M. S. Wong. *AIChE J.* **59**, 4474 (2013).
- [25] M. Martín-Martínez, L. M. Gómez-Sainero, J. Bedia, A. Arevalo-Bastante, J. J. Rodríguez. *Appl. Catal. B* **184**, 55 (2016).
- [26] V. A. Yakovlev, V. I. Simagina, S. N. Trukhan, V. A. Likholobov. *Kinet. Catal.* **41**, 25 (2000).
- [27] E. S. Lokteva, S. A. Kachevskii, A. O. Turakulova, E. V. Golubina, V. V. Lunin, A. E. Ermakov, M. A. Uimin, A. A. Mysik. *Russ. J. Phys. Chem. A* **83**, 1300 (2009).
- [28] T. N. Rostovshchikova, M. I. Shilina, E. V. Golubina, E. S. Lokteva, I. N. Krotova, S. A. Nikolaev, K. I. Maslakov, D. A. Yavsin. *Russ. Chem. Bull.* **64**, 812 (2015).
- [29] M. A. Keane, S. Gómez-Quero, F. Cárdenas-Lizana, W. Shen. *ChemCatChem* **1**, 270 (2009).
- [30] V. M. Kozhevnikov, D. A. Yavsin, V. M. Kouznetsov, V. M. Busov, V. M. Mikushkin, S. Y. Nikonov, S. A. Gurevich, A. Kolobov. *J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. Process. Meas. Phenom.* **18**, 1402 (2000).
- [31] C. A. Schneider, W. S. Rasband, K. W. Eliceiri. *Nat. Methods* **9**, 671 (2012).
- [32] F. Cárdenas-Lizana, S. Gómez-Quero, C. Amorim, M. A. Keane. *Appl. Catal. A Gen.* **473**, 41 (2014).
- [33] P. Miegge, J. L. Rousset, B. Tardy, J. Massardier, J. C. Bertolini. *J. Catal.* **149**, 404 (1994).
- [34] A. Nash, P. Nash. *Bull. Alloy Phase Diagr.* **5**, 446 (1984).
- [35] A. Zaleska-Medynska, M. Marchelek, M. Diak, E. Grabowska. *Adv. Colloid Interfac. Sci.* **229**, 80 (2016).
- [36] J. Zhang, H. Xu, X. Jin, Q. Ge, W. Li. *Appl. Catal. A Gen.* **290**, 87 (2005).
- [37] M. C. Biesinger, B. P. Payne, L. W. M. Lau, A. Gerson, R. S. C. Smart. *Surf. Interface Anal.* **41**, 324 (2009).
- [38] J. L. Rogers, M. C. Mangarella, A. D. D'Amico, J. R. Gallagher, M. R. Dutzer, E. Stavitski, J. T. Miller, C. Sievers. *ACS Catal.* **6**, 5873 (2016).
- [39] Y. Jiang, J. Chen, J. Zhang, Y. Zeng, Y. Wang, F. Zhou, M. Kiani, R. Wang. *Appl. Surf. Sci.* **420**, 214 (2017).
- [40] T. H. Gardner, D. Shekhawat, D. A. Berry, M. W. Smith, M. Salazar, E. L. Kugler. *Appl. Catal. A Gen.* **323**, 1 (2007).
- [41] C. Jiménez-González, Z. Boukha, B. de Rivas, J. R. González-Velasco, J. I. Gutiérrez-Ortiz, R. López-Fonseca. *Energy Fuels* **28**, 7109 (2014).
- [42] A. Aznarez, A. Gil, S. A. Korili. *RSC Adv.* **5**, 82296 (2015).
- [43] F. B. Noronha, M. C. Durão, M. S. Batista, L. G. Appel. *Catal. Today* **85**, 13 (2003).
- [44] M. D. Navalikhina, N. E. Kavalerskaya, E. S. Lokteva, A. A. Peristy, E. V. Golubina, V. V. Lunin. *Russ. J. Phys. Chem. A* **86**, 1669 (2012).
- [45] K. Morikawa, T. Shirasaki, M. Okada. in *Advances in Catalysis*, D. D. Eley, H. Pines, P. B. Weisz (Eds.), pp. 97–133, Academic Press, New York (1969).
- [46] P. Kim, H. Kim, J. B. Joo, W. Kim, I. K. Song, J. Yi. *J. Mol. Catal. A Chem.* **256**, 178 (2006).
- [47] P. Tian, L. Ouyang, X. Xu, C. Ao, X. Xu, R. Si, X. Shen, M. Lin, J. Xu, Y.-F. Han. *J. Catal.* **349**, 30 (2017).
- [48] J. T. Miller, B. L. Meyers, F. S. Modica, G. S. Lane, M. Vaarkamp, D. C. Koningsberger. *J. Catal.* **143**, 395 (1993).
- [49] S. Mukherjee, B. Ramalingam, S. Gangopadhyay. *J. Mater. Chem. A* **2**, 3954 (2014).
- [50] A. Y. Stakheev, L. M. Kustov. *Appl. Catal. A Gen.* **188**, 3 (1999).

Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/pac-2018-0207>).