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Liquid-phase hydrogenation of benzaldehyde over Pd-Ru/C catalysts: Synergistic effect between supported metals

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ABSTRACT

Bimetallic Pd-Ru/C catalysts prepared with different carbon supports were shown to be much more active in the liquid-phase hydrogenation of benzaldehyde in comparison with their monometallic analogs. In the case of systems based on nanoglobular carbon, the synergistic effect manifested itself as an increased selectivity for benzyl alcohol (86–90%) at a complete conversion of benzaldehyde, whereas the catalysts containing carbon nanotubes were highly active in hydrogenolysis of the $\mathrm{C{-}O}$ bonds, which caused an increased yield of toluene (up to 56%). The synergistic effect between palladium and ruthenium in the reaction under study can be related to the changes in the electronic and dispersion state of the supported metals upon interaction with each other and formation of Pd-Ru alloy. In terms of the electronic factor, the enhanced catalytic performance of bimetallic systems can be a result of facilitation of electrophilic activation of the $\mathrm{C{=}O}$ bond in benzaldehyde owing to an increased fraction of the electron-deficient palladium species. The nature of carbon support was shown to affect the electronic state of supported metals and thus catalytic properties of bimetallic Pd-Ru/C systems.

1. Introduction

The catalytic hydrogenation of benzaldehyde is used in industry for the production of benzyl alcohol, which is an important intermediate in the synthesis of vitamins, pharmaceuticals, pesticides, fragrances, and various esters [1–4]. Much attention is given now to the development of efficient catalysts for selective hydrogenation of benzaldehyde to benzyl alcohol. Various supported catalysts containing platinum [1–3], palladium [4–9], ruthenium [10–14] and nickel [15–18] were proposed to perform this reaction under mild conditions. Commercial palladium catalysts demonstrate high activity and retain their properties after multiple uses in protic solvents. The main drawback of these catalysts in hydrogenation of benzaldehyde is related to the fact that their selectivity for benzyl alcohol is not always high owing to hydrodeoxygenation into toluene [5,6,9,19]. The problem of selective reduction of the carbonyl group to the alcohol one (especially if the $\mathrm{C{=}C}$ bonds are present in a substrate molecule) is commonly solved with the use of platinum or ruthenium catalysts [3,11–13,20,21]. The latter catalysts are most attractive due to a relatively low cost of ruthenium compared to other noble metals [22]. However, the application of ruthenium catalysts for hydrogenation of aromatic aldehydes or ketones does not ensure a complete conversion of the initial compounds [13,14], and the hydrogenation of aromatic ring often occurs, which decreases the yield of the target alcohol [10,20,23].

At the same time, the development of supported bimetallic catalysts is still of interest because the introduction of the second, less expensive metal makes it possible to lower the catalyst cost and retain or even improve the catalytic properties [24–28]. Bimetallic composites often demonstrate the synergistic effect, i.e. the activity (or selectivity) of a bimetallic catalyst is greater than the sum of activities (or selectivities) of its monometallic analogs. The synergistic effect was found, in particular, when studying the palladium-ruthenium catalysts in hydrogenation of

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1-hexene [29], benzene [30], *o*-xylene [31], 1,4-butanediol [32,33], phenol [33,34], anisole [33], cinnamaldehyde [35], benzoic acid [36], dimethyl terephthalate [37], 2-methyl-2-nitropropane [38], *p*-chloronitrobenzene [39], pyridine [33], and glucose [40]. However, the Pd-Ru composites remain poorly investigated among numerous bimetallic catalysts [25,27].

In the synthesis of a catalyst with specified activity and selectivity, of key importance are not only the nature of a metal component and its state in the catalyst but also features of the support. The application of carbon materials as supports in the synthesis of hydrogenation catalysts has some advantages. Carbon supports have a high specific surface area, a developed pore space that ensures a transfer of reactants and reaction products, controllable chemical properties of the surface, and chemical inertness, especially in strong acids and bases [41–46]. Ding et al. [12] proposed the mesoporous carbon-based supported catalysts, which are highly active in hydrogenation of benzaldehyde and provide a nearly 100% selectivity for benzyl alcohol. Nevertheless, revealing the effect of the carbon support features (pore structure, chemical composition and surface morphology) on the formation, chemical state, size and catalytic properties of metal sites remains a topical problem.

The present work deals with the study of Pd-Ru/C catalysts prepared with the use of different carbon supports in the liquid-phase hydrogenation of benzaldehyde. Multi-wall carbon nanotubes (CNTs) and nanoglobular carbon (NGC), which were characterized in our earlier works [9,14,47], served as the supports. The chosen carbon materials differ fundamentally in the preparation method, structure, and such physicochemical characteristics as texture and acid-base properties of the surface. It was shown that the bimetallic Pd-Ru/C catalysts exhibited a substantially enhanced hydrogenation activity compared with the monometallic analogs (Pd/C and Ru/C). To reveal the reason of synergistic effect between palladium and ruthenium in the tested reaction, the samples were characterized by temperature-programmed reduction (H_2-TPR), pulsed chemisorption of CO, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

The catalysts were synthesized using CNTs Baytubes® C 150 HP purchased from Bayer MaterialScience AG (Leverkusen, Germany) and NGC represented by conductive carbon black P278-E (analog to N472) and supplied by Experimental Technology Department of Institute of Hydrocarbons Processing (Omsk, Russia). Prior to experiments, the carbon supports were dried overnight in air at 393 K to remove the adsorbed water.

Bimetallic Pd-Ru catalysts with the total content of supported metals close to 1.5 wt.% were obtained by incipient wetness impregnation of the carbon supports. To prepare the impregnating solutions, palladium (II) chloride and ruthenium (IV) hydroxytrichloride (both pure grade, JSC “Aurat”) were dissolved in concentrated hydrochloric acid (Pd to HCl and Ru to HCl molar ratios of 1:2 and 1:3, respectively) and diluted with water to a desired concentration. Prior to impregnation, the Pd- and Ru-containing solutions were mixed so as to reach the Ru:Pd molar ratios of 1 and 2.5 in the resulting samples. The corresponding samples are denoted hereinafter as 1Pd-1Ru/C and 2Pd-5Ru/C. Data on their composition are listed in Table 1. After the impregnation, the samples were dried in air at room temperature.

2.2. Catalyst characterization

Palladium and ruthenium contents in the catalysts were estimated by optical emission spectrometry with inductively coupled plasma (ICP-OES) on a Varian 710-ES spectrometer. The measurements were made after the dissolution of catalyst samples in a mixture of nitric and hydrochloric (or perchloric) acids.

After deposition of the precursors on the supports and drying in air at room temperature, the samples were examined by H_2-TPR using an AutoChem II 2920 (Micromeritics) chemisorption analyzer equipped with a thermal conductivity detector (TCD). The H_2-TPR experiments were performed with a mixture of 10% H_2 and argon (the flow rate 25 $cm^3\,min^{-1}$) in a temperature range of 308–673 K at a heating rate of 10 $K\,min^{-1}$.

The dispersion of a supported metal in the catalysts was estimated by pulse chemisorption of CO after the reduction in flowing hydrogen at 523 K and cooling in an inert gas to room temperature. A mixture of 10% CO and helium was fed into the flow of inert carrier gas (helium) by pulses at equal time intervals. The batching was carried out at room temperature until the TCD signal became constant. The dispersion was calculated taking into account the average adsorption stoichiometry: CO:Pd = 0.5 and CO:Ru = 1 [6,47–49].

TEM images of the catalysts pre-reduced at 523 K were taken by a JEM-2100 (JEOL) instrument using an accelerating voltage of 200 kV. The samples were prepared by dispersing the catalysts in ethanol and spraying the suspension on a perforated carbon-coated copper grid. The energy dispersive X-ray analysis (EDX) was performed with an INCA 250 (Oxford Instruments) spectrometer. TEM images were analyzed using DigitalMicrograph (Gatan) software.

XPS measurements of the catalysts were carried out on a SPECS spectrometer at a residual pressure of 7×10^{-7} Pa in the analyzer chamber. Before the measurements, the samples were reduced in a hydrogen flow at 523 K. The spectra were recorded using monochromatic Al*K*α radiation ($h\nu = 1486.7$ eV). Preliminarily, the binding energy (BE) scale of the spectrometer was calibrated against signals obtained from metallic gold and copper, Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.6 eV). The spectra were calibrated with respect to C 1*s* line of the carbon support (284.6 eV). The measurement data were processed using the XPSPEAK software. The Gaussian-Lorentzian function with the fixed value of Gaussian/Lorentzian ratio (Gaussian 30%) was used for deconvolution of the spectra. During the fitting procedure, the parameters of each component such as intensity, full width at half maximum and peak position were varied within a reasonable range [50].

2.3. Catalytic measurements

Pretreatment of the catalyst samples prior to catalytic experiments included drying in argon flow at 423 K for 0.5 h and reduction in flowing hydrogen at 523 K for 2 h.

The liquid-phase hydrogenation of benzaldehyde (98%, Acros Organics) in the presence of the synthesized catalysts was studied using a 180 cm^3 steel autoclave. A 500-mg catalyst sample was placed into the autoclave with 30 cm^3 of ethanol (95%). Air components were removed from the catalyst pore space by pre-reduction with hydrogen at a temperature of 353 K and a pressure of 0.5 MPa for 1 h. The reaction mixture was heated to a specified temperature by circulation of heated water through the external jacket. To stir the mixture, the autoclave was mounted on a shaker.

After pre-reduction, 5.0 cm^3 of benzaldehyde and 65 cm^3 of ethanol were loaded into the autoclave. The hydrogenation was carried out for 5 h at a temperature of 313 K and a hydrogen pressure of 0.5 MPa under vigorous stirring of the reaction mixture, which excluded external diffusion limitations. The reaction products were identified by gas chromatography-mass spectrometry (GC–MS) on an Agilent 5973N/6890N instrument. The quantitative

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Table 1
Designation and composition of bimetallic catalysts.

Sample	Pd content (wt.%)[a]	Ru content (wt.%)[a]	Total content of metals (wt.%)	Ru:Pd molar ratio
1Pd-1Ru/NGC	0.81 ± 0.05	0.76 ± 0.05	1.57	1.0
2Pd-5Ru/NGC	0.48 ± 0.01	1.15 ± 0.07	1.63	2.5
1Pd-1Ru/CNTs	0.85 ± 0.02	0.80 ± 0.05	1.65	1.0
2Pd-5Ru/CNTs	0.49 ± 0.01	1.22 ± 0.02	1.71	2.6

[a] According to optical emission spectrometry with inductively coupled plasma (ICP-OES).

composition of the liquid phase in the autoclave was determined every hour using gas chromatography (GC) on a Hewlett Packard 5890 Series II chromatograph equipped with a capillary column HP-PONA (50 m × 0.20 mm, Agilent Technologies) and a flame ionization detector.

3. Results and discussion

Pd-Ru/NGC and Pd-Ru/CNTs catalysts with the total content of supported metals 1.6–1.7 wt.% and the Ru:Pd molar ratio of 1.0 or 2.5 (Table 1) were studied in the hydrogenation of benzaldehyde in ethanol medium at a temperature of 313 K and hydrogen pressure of 0.5 MPa. Results of the catalytic measurements were compared with the data obtained under identical conditions for monometallic catalysts Pd/CNTs, Pd/NGC, Ru/CNTs and Ru/NGC containing 1.5 wt.% of palladium or ruthenium. Besides, the catalytic behavior of monometallic samples (1Pd/C, 1Ru/C) with a metal loading close to a loading of one of the metal in 1Pd-1Ru/C samples (about 1 wt.%) was taken into account.

All the samples of bimetallic catalysts showed high activity in the tested reaction, and a complete conversion of benzaldehyde was already observed 1 h after the onset of the reaction (Table 2). Under the same reaction conditions, only the Pd/NGC sample showed a comparable activity (benzaldehyde conversion of 99%), whereas Pd/CNTs, Ru/CNTs and Ru/NGC catalysts gave a conversion of benzaldehyde equal to about 32, 40 and 43%, respectively.

Under the indicated conditions of catalytic hydrogenation, the products of benzaldehyde transformations were benzyl alcohol, toluene, (ethoxymethyl)benzene and (diethoxymethyl) benzene, which are formed according to Scheme 1.

Joint transformations of benzaldehyde or benzyl alcohol with a solvent yielding (ethoxymethyl)benzene and (diethoxymethyl)benzene may involve acid sites of the support [5,9,14] or electron-deficient species of the supported metal [51,52]. It should be noted that in the case of bimetallic catalysts the transformation sequence benzaldehyde → benzyl alcohol → toluene prevailed, while the formation of side ethers was virtually suppressed: the yield of (ethoxymethyl)benzene did not exceed 3% and (diethoxymethyl)benzene was not detected among the products (Table 2).

As follows from analysis of catalytic measurements (Table 2), in distinction to monometallic NGC-supported samples, bimetallic catalysts prepared with the same support were highly selective for benzyl alcohol (86–90%) under the chosen conditions of the reaction (313 K, 1 h). In the process, hydrogenolysis of the C—O bonds was much less pronounced in comparison with the Pd/NGC sample; as a result, the toluene yield was not high (up to 10%).

In the presence of Pd-Ru/NGC catalysts, extending the reaction time increased the fraction of toluene in the products up to 90% (Fig. S1a and b in the Supplementary materials). At the same time, an increase in the Ru:Pd ratio in the NGC-supported bimetallic system made it possible to diminish the degree of hydrodeoxygenation and raise the yield of benzyl alcohol. Thus, owing to hydrogenation of benzaldehyde in the presence of 1Pd-1Ru/NGC sample, mole fractions of benzyl alcohol and toluene were equal to 0.06 and 0.93, respectively, 4 h after the beginning of the experiment (Fig. S1a). Under the same conditions, the 2Pd-5Ru/NGC catalyst showed a higher selectivity for benzyl alcohol, whose mole fraction reached 0.35, whereas the fraction of toluene decreased to 0.64 (Fig. S1b).

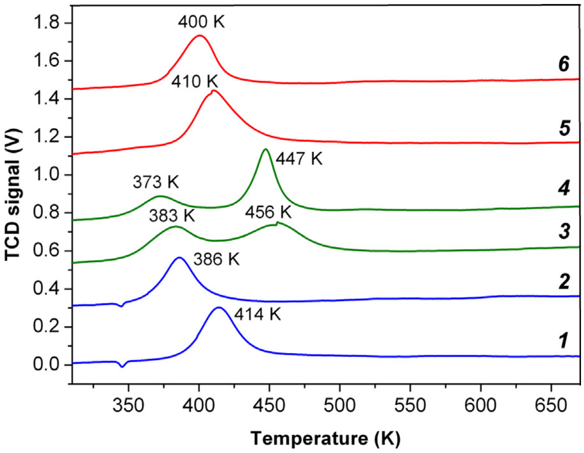

Fig. 1. The H_2-TPR profiles of supported chloride precursors in the samples: Pd/NGC (1), Pd/CNTs (2), Ru/NGC (3), Ru/CNTs (4), Pd-Ru/NGC (5), Pd-Ru/CNTs (6). Prior to measurements, the samples were dried in air at room temperature.

Under the specified conditions of the reaction (313 K, 1 h), CNTs-based bimetallic catalysts showed an increased activity in hydrodeoxygenation, which is comparable with the activity of Pd/NGC sample (Table 2). As a result, the selectivity for benzyl alcohol was lower as compared to NGC-based catalysts: about 42 and 57% for samples 1Pd-1Ru/CNTs and 2Pd-5Ru/CNTs, respectively, and the yield of toluene reached 56%.

In the presence of Pd-Ru/CNTs catalysts, the degree of hydrodeoxygenation was even higher in comparison with bimetallic NGC-supported samples: as the reaction time increased, the fraction of toluene in the products reached 100% (Fig. S1c and d). Therewith, an increase of the Ru:Pd ratio in the bimetallic catalyst ensured a pronounced growth of selectivity for benzyl alcohol only at the beginning of the experiment.

The catalytic properties of 1Pd-1Ru/C catalysts were additionally compared to those of monometallic 1Pd/C and 1Ru/C catalysts containing almost the same amount of Pd and Ru (1 wt.%) as bimetallic samples (Table S1). Under the same reaction conditions, the bimetallic catalysts were superior in hydrogenation activity, i.e. a conversion of benzaldehyde over 1Pd-1Ru/C catalysts is greater than the sum of conversions over 1Pd/C and 1Ru/C. As compared to monometallic catalysts, 1Pd-1Ru/NGC sample demonstrated an increased yield of benzyl alcohol, whereas 1Pd-1Ru/CNTs catalyst was highly active in hydrogenolysis of the C—O bonds, which produced a high yield of toluene.

To elucidate the causes of the increased hydrogenation activity of bimetallic catalysts, the formation of metallic sites was studied by H_2-TPR. The dispersion state of formed metal nanoparticles (NPs) was examined by pulsed chemisorption of CO and TEM. The H_2-TPR profiles of monometallic Pd/C samples show a single hydrogen consumption peak corresponding to the reduction of supported palladium chloride complexes (Fig. 1, curves 1 and 2).

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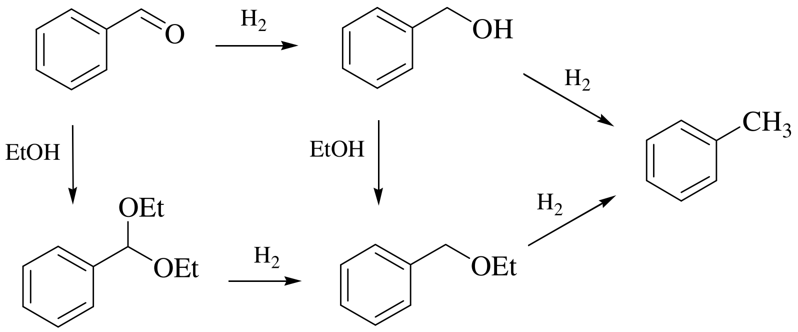
Table 2
Catalytic properties of Pd/C, Ru/C and Pd-Ru/C samples in the liquid-phase hydrogenation of benzaldehyde under the hydrogen pressure[a]. Prior to experiments, the catalysts were dried in argon at 423 K for 0.5 h and reduced in flowing hydrogen at 523 K for 2 h.

Catalyst[b]	*D*[c]	*d* (nm)[d]	*X* (%)[e]	*S* (%)[f]			
				BA	T	EMB	DMB
Pd/NGC	0.16	n.d.	99.3	41.9	52.0	4.9	0
1Pd-1Ru/NGC	0.79	~1	100	86.3	10.2	2.8	0
2Pd-5Ru/NGC	0.69	~1	100	89.6	7.6	2.2	0
Ru/NGC	0.62	1.3	43.1	43.7	0.2	0	49.9
Pd/CNTs	0.36	2.3	31.6	82.8	0.2	0.9	12.6
1Pd-1Ru/CNTs	0.54	1.6	100	41.5	56.0	2.1	0
2Pd-5Ru/CNTs	0.43	1.6	100	57.4	39.7	2.2	0
Ru/CNTs	0.30	1.8	39.6	80.6	0.6	0	18.0

[a] Reaction conditions: temperature of 313 K, pressure of 0.5 MPa, 1 h, 95 cm^3 of ethanol, 5.0 cm^3 of C_6H_5CHO, 500 mg of catalyst.
[b] The total content of supported metals in all catalysts is constant and close to 1.5 wt.%.
[c] The metal dispersion determined by pulsed chemisorption of CO after H_2-TPR. The calculation used the following adsorption stoichiometry: CO:Pd = 0.5, CO:Ru = 1 [6,47–49].
[d] The average size of supported metal particles estimated by TEM.
[e] Conversion of benzaldehyde according to GC.
[f] Selectivities for benzyl alcohol (BA), toluene (T), (ethoxymethyl)benzene (EMB) and (diethoxymethyl)benzene (DMB) according to GC.



Scheme 1. Reaction pathways of benzaldehyde hydrogenation in ethanol medium.

Therewith, a precursor in Pd/NGC sample is reduced under more severe conditions (a temperature maximum at 414 K), which leads to the formation of NPs with a lower dispersion as compared with Pd/CNTs (Table 2). According to TEM measurements [47], the palladium NPs in Pd/CNTs sample have the average size of 2.3 nm (Table 2, Fig. S2a). Unfortunately, it was not possible to accurately determine the average particle size of Pd in the Pd/NGC sample because of very blurred edges of the NPs in TEM images.

At least two hydrogen consumption regions can be distinguished on the H_2-TPR profiles of ruthenium catalysts (Fig. 1, curves 3 and 4); they may correspond to the reduction of supported ruthenium compounds having different composition (the hydrolysis products) or degree of their interaction with the support. The reductions occur nearly identically in Ru/NGC and Ru/CNTs that may be due to a close composition of the surface complexes in these samples. However, in distinction from Ru/CNTs, the Ru/NGC sample has a higher fraction of species which are more stable to reduction, i.e., stronger bound to the support surface, since the temperature maxima of H_2-TPR peaks are shifted toward high temperatures. Assessment of the dispersion by pulsed CO chemisorption showed that the reduction of a precursor in the Ru/NGC sample results in the formation of ruthenium NPs with a higher dispersion in comparison with Ru/CNTs (Table 2). According to microscopic measurements [14], Ru/NGC sample contains ruthenium NPs with a denser location and better dispersion as compared to Ru/CNTs that is in agreement with CO chemisorption data. The average particle sizes are determined to be around 1.8 and 1.3 nm for Ru/CNTs and Ru/NGC, respectively (Table 2, Fig. S2b and c).

The H_2-TPR profiles of bimetallic samples (Fig. 1, curves 5 and 6) have a single hydrogen consumption region (the temperature maximum near 400 K) and resemble the H_2-TPR curves of palladium samples. The supported palladium compounds are likely to accelerate the reduction of ruthenium precursor; as a result, the high-temperature peak (near 450 K) typical of monometallic ruthenium catalysts is shifted toward low-temperature region and overlaps with the peak corresponding to the reduction of palladium compounds. A simultaneous reduction in the case of supported palladium-ruthenium systems is confirmed by the data reported in [34,36,37] and indicates the mutual interaction of palladium and ruthenium compounds and the formation of bimetallic NPs. As shown by a comparison of CO chemisorption data for the samples prepared with the same support, the dispersion of NPs in bimetallic samples is noticeably higher in comparison with the corresponding monometallic systems (Table 2). As can be seen from TEM images of Pd-Ru/C samples (Fig. 2), the bimetallic NPs have a spherical shape, and the average particle size is somewhat less than that of monometallic systems regardless of the nature of carbon support (Table 2). So, the results of TEM measurements are rather in agreement with CO chemisorption data.

An increased dispersion caused by the interaction in the supported Pd-Ru system can be a reason of the observed synergistic effect in benzaldehyde hydrogenation because, firstly, a decrease in the size of metal NPs increases the fraction of active sites accessible to reactants and, secondly, the presence of the second metal prevents aggregation of the NPs during the catalyst pretreatment and in the course of reaction [34,36,37]. Noteworthy is the fact that dispersion of the NPs in bimetallic catalysts is affected by the nature of the carbon support. The Pd-Ru/CNTs samples have a much lower dispersion than NGC-based bimetallic catalysts. In the latter case, there are well-dispersed NPs with very homogeneous size distribution and average size of about 1 nm (Fig. 2a and b, Table 2).

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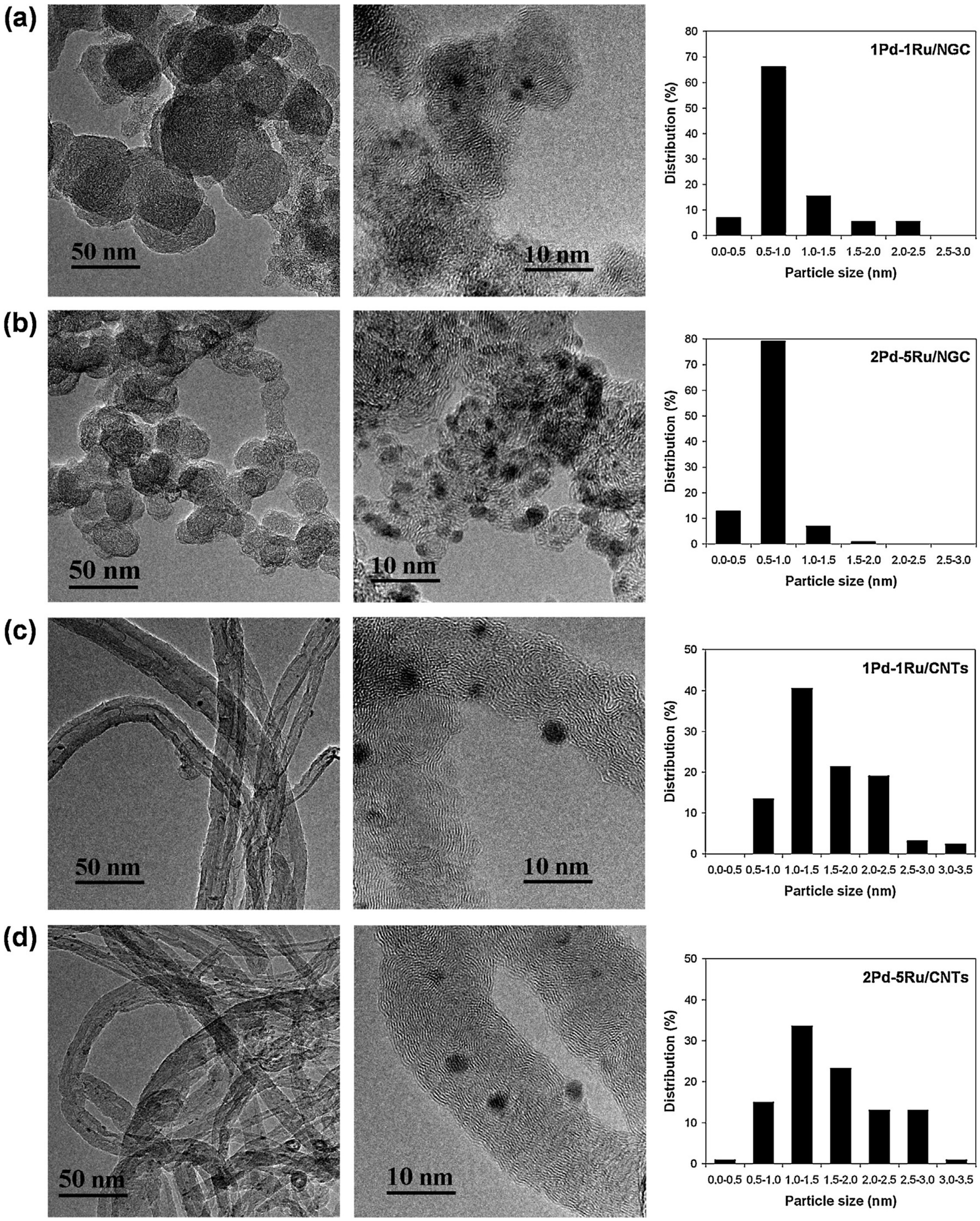

Fig. 2. Representative TEM images of Pd-Ru bimetallic samples at different magnifications: 1Pd-1Ru/NGC (a), 2Pd-5Ru/NGC (b), 1Pd-1Ru/CNTs (c), 2Pd-5Ru/CNTs (d). The particle size distribution histograms are also presented. Prior to measurements, the samples were reduced in flowing hydrogen at 523 K.

To clarify the question of whether the Pd-Ru alloy is formed upon interaction of metals, high resolution TEM (HRTEM) images and EDX spectra were additionally obtained. As shown by HRTEM analysis (Fig. 3a), reduced 1Pd-1Ru/CNTs sample contains NPs with a *d*-spacing of 0.217 nm. This value does not correspond to any lattice spacings of palladium or ruthenium and very close to that of Pd-Ru alloy (0.219 nm [53]). The EDX spectrum (Fig. 3b) recorded from the region shown in Fig. 3a includes signals corresponding to palladium and ruthenium. In very rare cases (Fig. S3), the Pd NPs with a *d*-spacing of 0.225 nm were observed in HRTEM images of the bimetallic sample. However, numerous micrographs and EDX spectra (as shown in Fig. 3) confirm that supported NPs are mostly bimetallic.

The palladium-ruthenium interaction in bimetallic systems was also revealed by XPS, which was employed to investigate the electronic state of supported palladium and ruthenium in the reduced catalysts. The Pd 3*d* spectra recorded for mono- and bimetallic catalysts show a typical Pd $3d_{5/2}$–Pd $3d_{3/2}$ doublet consisting of two overlapping components (Fig. 4), which indicates that the supported palladium has two electronic states. The positions of the signals with lower BE values (335.9-336.4 eV in the $3d_{5/2}$ region, Table 3) are close to those observed for metallic palladium

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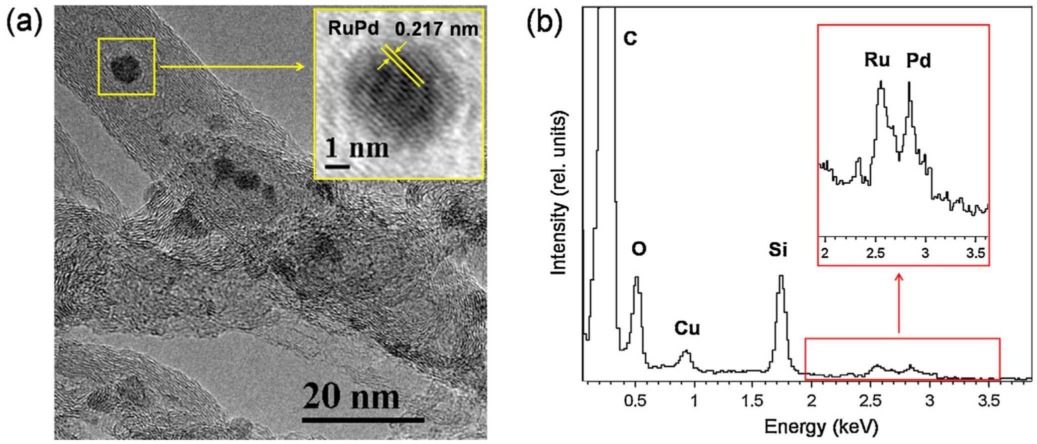

Fig. 3. HRTEM image of 1Pd-1Ru/CNTs sample (a) and EDX spectrum recorded from the region shown in micrograph (b).

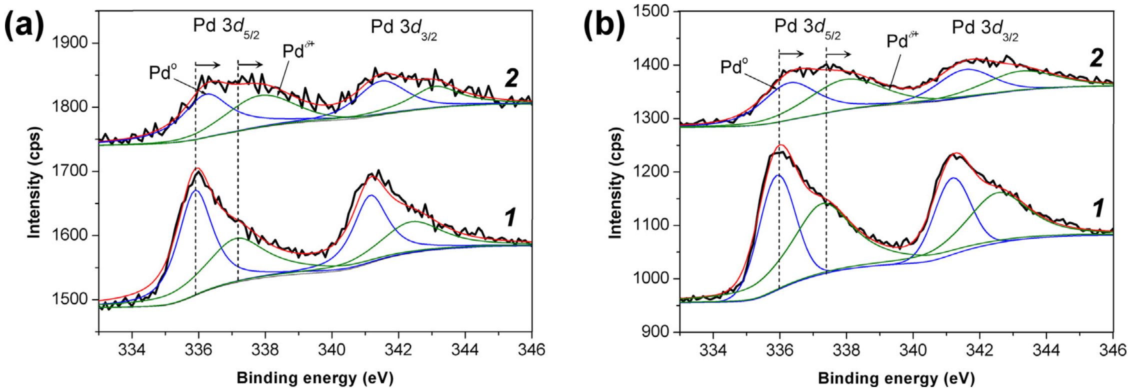

Fig. 4. Pd 3*d* spectra of Pd/C (1) and 1Pd-1Ru/C (2) catalysts prepared with the use of NGC (a) and CNTs (b). Prior to measurements, the samples were reduced in flowing hydrogen at 523 K.

Table 3
Results of XPS analysis of Pd/C, Ru/C and 1Pd-1Ru/C catalysts.

Sample	BE of Pd $3d_{5/2}$ (eV)		BE of Ru $3p_{3/2}$ (eV)	Atomic ratios	
	Pd^0	$Pd^{\delta+}$	$Ru^{\delta+}$	Pd^0:$Pd^{\delta+}$	Pd:C
Pd/NGC	335.9	337.2	–	1.3	0.0016
Pd/CNTs	336.2	337.9	–	1.0	0.0031
1Pd-1Ru/NGC	336.3	338.0	462.5	1.1	0.0007
1Pd-1Ru/CNTs	336.4	338.2	462.2	0.7	0.0021
Ru/NGC	–	–	462.7	–	–
Ru/CNTs	–	–	462.5	–	–

(BE = 335.7 ± 0.3 eV [54,55]), while the signals with higher BE values (337.2-338.2 eV in the $3d_{5/2}$ region, Table 3) can be attributed to the electron-deficient palladium species $Pd^{\delta+}$ (BE = 337.9 ± 0.3 eV for $PdCl_2$ [54,55]). Since the signals from ruthenium in the Ru 3*d* region overlap with the C 1*s* line from the support, Ru $3p_{3/2}$ peak was employed to estimate the electronic state of ruthenium in mono- and bimetallic samples [36,56,57].

As shown by analysis of XPS spectra, an obvious shift (by 0.2–0.8 eV) of the maxima of Pd^0 and $Pd^{\delta+}$ lines toward high BE values and a decrease in the Pd^0:$Pd^{\delta+}$ atomic ratio are observed for 1Pd-1Ru/C with respect to Pd/C catalyst based on the same support (Fig. 4, Table 3). At the same time, a negative shift (0.2 or 0.3 eV) of Ru $3p_{3/2}$ peak occurs for 1Pd-1Ru/C with respect to monometallic analog Ru/C (Fig. 5, Table 3). In the case of 1Pd-1Ru/CNTs catalyst, the Ru $3p_{3/2}$ signal can be assigned to metallic ruthenium (BE = 462.2 eV [57]). Such changes in the electronic state of supported palladium and ruthenium in bimetallic Pd-Ru system have been observed earlier [34,36] and can be caused by the mutual interaction of metals during joint reduction of supported precursors (see Fig. 1) and the formation of Pd-Ru alloy (see Fig. 3). The direction of electron transfer (from palladium to ruthenium) is possibly related to a greater surface electronegativity of ruthenium in comparison with palladium [58]. This effect is contrary to that seen in bulk, possibly as a result of the anisotropic character of a surface that modifies the relative electronegativities of the metal atoms.

Thus, the synergistic effect between palladium and ruthenium in hydrogenation of benzaldehyde can be caused by the mutual interaction of supported metals and the formation of alloy, which (1) increases the dispersion and thus the fraction of accessible active sites on which hydrogen adsorption is facilitated, (2) changes the electronic state of metals and therefore promotes the activation of hydrogen and substrate molecules. In terms of the electronic factor, it is somewhat difficult to unequivocally establish a participation of palladium and ruthenium species as active sites in the tested reaction. The most plausible mechanism of promoting action of the second metal involves the formation of so-called mixed sites where both metal components participate in the catalytic transformations, but one of them is not fully reduced in the running conditions of the reaction [59,60]. In this case, the promotion effect is due to the presence of electron-deficient species which enhance the polarization of $C{=}O$ bond and activation of hydrogen. The electron transfer from palladium to a more electronegative ruthenium increases the fraction of electron-deficient palladium species in the catalysts, which serve as the electrophilic sites of adsorption and activation of the $C{=}O$ bond in the benzaldehyde molecule (Fig. 6). The most possible ways of electrophilic activation of the carbonyl group on these sites may involve the η^1-(O) and η^2-(C,O) modes

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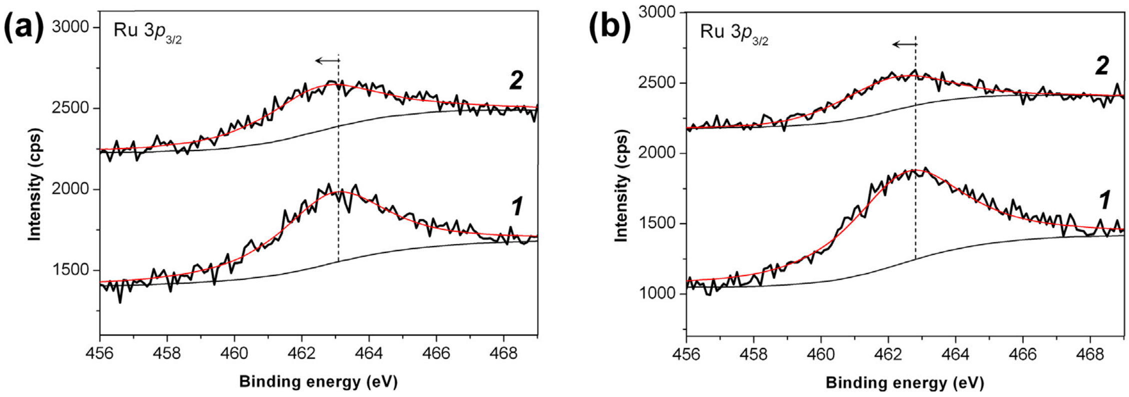

Fig. 5. Ru $3p_{3/2}$ spectra of Ru/C (1) and 1Pd-1Ru/C (2) catalysts prepared with the use of NGC (a) and CNTs (b). Prior to measurements, the samples were reduced in flowing hydrogen at 523 K.

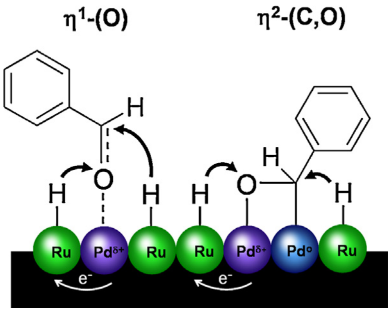

Fig. 6. The proposed mechanism of promoting action of the second metal in bimetallic Pd-Ru/C catalysts and the preferential modes of benzaldehyde activation on their surface.

in which the C═O bond is weakened, thus facilitating a subsequent addition of chemisorbed hydrogen [61].

The differences in the catalytic properties of bimetallic samples synthesized with different supports can also be related to changes in the electronic state of supported metals. An increased activity of the CNTs-containing catalysts in hydrodeoxygenation into toluene (Table 2, Fig. S1, Table S1) is apparently caused by a stronger interaction in the Pd-Ru system, which decreases the Pd^0:$Pd^{\delta+}$ ratio (Table 3). Besides, due to electron transfer from palladium to ruthenium, the latter is present in the 1Pd-1Ru/CNTs catalyst as Ru^0. It is known that activation of the hydrogen molecule and cleavage of the H—H bond are less hindered if the metallic sites have an increased number of accessible electrons at the external *d*-orbital [62]. So, the preferential sites of hydrogen adsorption and activation are represented most likely by the electron-rich supported ruthenium species whose fraction can increase with raising the Ru:Pd ratio. Although CNTs-based bimetallic catalysts have a much lower dispersion than NGC-based samples, the adsorption ability of metal sites in Pd-Ru/CNTs catalysts with respect to reactants can be increased due to the higher fraction of $Pd^{\delta+}$ and Ru^0. This leads to a deeper hydrogenation and increase in the toluene yield. The described effect may be related to the features of CNTs affecting the interaction in bimetallic system (composition of the surface functional cover and electrical conductivity) and requires more detailed investigation.

The mechanism considered above can explain the observed synergistic effect and is corroborated by some works on selective hydrogenation of cinnamaldehyde in the presence of supported bimetallic systems Ru-Sn [63], Rh-Sn [64], Pd-Sn [65], Pd-Ru [35], Pt-Sn [61], Pt-Fe [66] and Pt-Ru [67].

4. Conclusions

Thus, bimetallic Pd-Ru/C catalysts synthesized with different carbon supports were shown to be much more active in the liquid-phase hydrogenation of benzaldehyde than their monometallic analogs. In the case of NGC-based systems, the synergistic effect shows up as an increased selectivity for the formation of benzyl alcohol (86–90%) at a complete conversion of benzaldehyde, whereas the catalysts prepared with the use of CNTs were highly active in hydrogenolysis of the C—O bonds, which caused an increased yield of toluene (up to 56%). The data obtained for the catalysts by H_2-TPR, pulsed CO chemisorption, TEM and XPS suggest that the synergistic effect between palladium and ruthenium in the tested reaction can be related to changes in the electronic and dispersion states of supported metals upon interaction with each other and formation of Pd-Ru alloy. In terms of the electronic factor, the enhanced catalytic performance of bimetallic systems can be caused by facilitation of electrophilic activation of the C═O bond in benzaldehyde owing to an increased fraction of electron-deficient palladium species. The nature of carbon support was shown to affect the electronic state of supported metals and thus catalytic properties of bimetallic Pd-Ru/C systems. Obviously, this effect may be related to the physicochemical features of each carbon support influencing the interaction in bimetallic system and requires more detailed investigation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2016.07.022.

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