

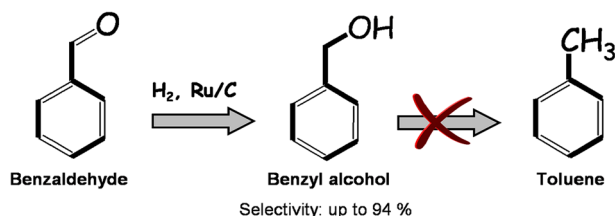
# Effects of the carbon support nature and ruthenium content on the performances of Ru/C catalysts in the liquid-phase hydrogenation of benzaldehyde to benzyl alcohol

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**Abstract** The hydrogenation of benzaldehyde in ethanol medium in the presence of Ru/C catalysts was shown to proceed with the preferential formation of benzyl alcohol without subsequent hydrodeoxygenation into toluene. An increase in ruthenium content of the catalysts from 0.3 to 1.5 % enhanced the catalytic activity at a high selectivity for benzyl alcohol. The effect of physicochemical characteristics of the support on the formation and catalytic properties of metallic sites in the Ru/C samples was revealed. Most active in the formation of benzyl alcohol were the catalysts containing carbon nanotubes.

*Graphical abstract*



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## Introduction

Benzyl alcohol is a valuable intermediate in the synthesis of vitamins, pharmaceuticals, pesticides, fragrances, and various esters. To produce benzyl alcohol, different methods of benzaldehyde reduction especially heterogeneous and homogeneous catalytic hydrogenation [1–6] and catalytic hydrogen transfer reactions [7–9] have been proposed. Among them, catalytic hydrogenation of benzaldehyde by hydrogen gas in the presence of supported metal catalysts remains one of the industrial processes for producing benzyl alcohol [1].

Presently, the development of efficient catalysts for selective hydrogenation of benzaldehyde to benzyl alcohol attracts considerable attention. To perform this reaction under mild conditions, many supported metal catalysts, such as Pt- [1, 3], Pd- [2, 10, 11], Ru- [12–15], and Ni-based [16–18] catalysts, have been suggested. Although supported platinum and palladium systems are used as industrial hydrogenation catalysts [1], interest in Ru-based catalysts is still unabated, since ruthenium demonstrates high activity in reduction of the carbonyl group of ketones and aldehydes and has the lowest cost among other platinum group metals [13–15, 19–22]. Undesired reaction pathways leading to toluene, i.e., the reactions benzaldehyde → toluene and benzaldehyde → benzyl alcohol → toluene, are frequently realized during hydrogenation of benzaldehyde over metal catalysts, especially Ni and Pd [8, 10, 11, 18].

In the synthesis of a catalyst with desired 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 as well as the methods of catalyst preparation and activation [21]. The use of carbon materials as supports in the synthesis of catalysts for liquid-phase hydrogenation has some advantages. Carbon supports possess a high specific surface area, a developed pore space, and controllable chemical properties of the surface [23–26]. Highly active carbon-based catalysts allowing to attain benzyl alcohol selectivity closed to 100 % have been proposed [14]. Nevertheless, the elucidation of the effect of carbon support nature (pore structure, chemical composition, and morphology of the surface) on the formation, chemical state, size, and catalytic properties of metallic sites is still a challenge.

Liquid-phase hydrogenation is widely employed in both the laboratory and industrial practice because it occurs under milder temperature conditions compared to the vapor-phase process, thus allowing the reduction of high-boiling, thermally unstable, and complex compounds. However, the composition of the liquid-phase hydrogenation products is strongly determined by the solvent nature [10, 12, 21, 27]. When the reaction is carried out in the presence of ruthenium catalysts, their sensitivity to the solvent composition should be taken into account. For example, in the study of ruthenium catalysts [21], the presence of water increased the hydrogenation rate. According to

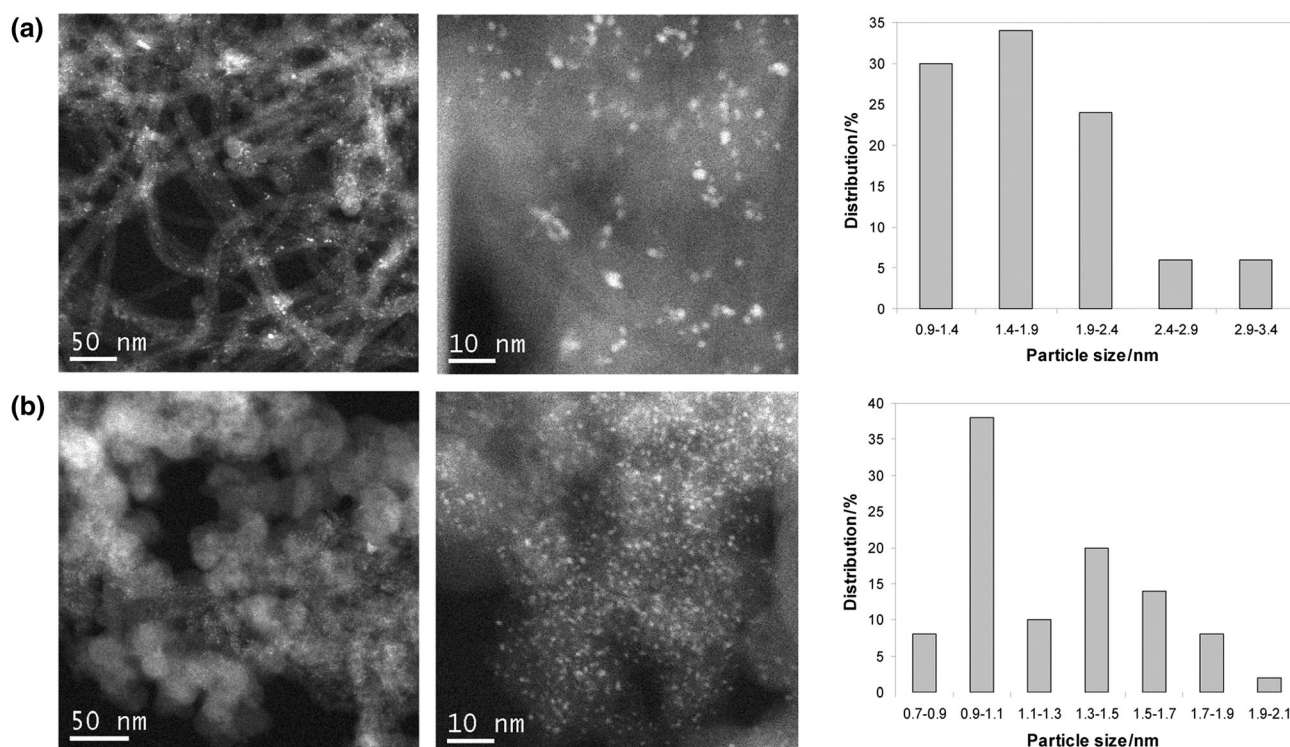
previous studies [28], aliphatic alcohols are the appropriate solvents for hydrogenation of benzaldehyde.

This work was aimed to reveal the effects of the carbon support nature and ruthenium content on the performance of Ru/C catalysts in selective hydrogenation of benzaldehyde to benzyl alcohol in ethanol medium. As the catalyst supports, we chose the carbon materials, multi-wall carbon nanotubes (CNT) and carbon black (CB), in principle differed in preparation method, structure, and physicochemical characteristics such as texture and surface acid–base properties.

## Results and discussion

As follows from high angular annular dark-field scanning transmission electron microscopic (STEM-HAADF) study (Fig. 1), chosen carbon materials have different morphologies: in distinction to CNT, the CB support consists of the aggregated globular particles.

The pore structure characteristics of CNT and CB were obtained from the conventional analysis of nitrogen adsorption–desorption isotherms. Both isotherms (Fig. S1a in the Supplementary Material) exhibit IV-type curves with an H3 hysteresis loop as defined by IUPAC [29]. This indicates that both CNT and CB have mesoporous structures with relatively uniform pores. Difference between CNT and CB



**Fig. 1** STEM-HAADF images of 1.5 % Ru/CNT (a) and 1.5 % Ru/CB (b) samples at different magnifications

involves the lower specific surface area of the CNT sample along with a large average pore size (Table 1). As can be seen from pore size distribution (PSD) curves (Fig. S1b in the Supplementary Material), both carbon materials have mainly 10–100 nm pores (96 % for CNT and 88 % for CB) with the maximum at 30–40 nm for CNT and without pronounced maximum in the case of CB. Unlike CNT, CB is characterized by larger amount of pores with a diameter less than 5 nm that provides higher specific surface area.

Earlier we estimated [30] the values of point of zero charge (PZC) of these carbon materials and found that the surface of CB is more acidic (PZC = 6.1) than the surface of CNT (PZC = 7.7). According to Fourier transform infrared (FTIR) spectroscopy (Fig. 2), the surface of CNT is extremely poor in the functional groups compared to CB. On the basis of literature data [31–33], it can be assumed that the surface of CB is characterized by the presence of phenol (C–O stretch at 1000–1220  $\text{cm}^{-1}$ ), ether (C–O–C stretch at 1150–1250  $\text{cm}^{-1}$ ), lactone (C–O stretch at 1160–1370  $\text{cm}^{-1}$  and at 1675–1790  $\text{cm}^{-1}$ ), quinone (C=O stretch at 1550–1680  $\text{cm}^{-1}$ ), carboxyl (C–O stretch at 1120–1200  $\text{cm}^{-1}$  and C=O stretch at 1665–1760  $\text{cm}^{-1}$ ), and anhydride (C–O stretch at 980–1300  $\text{cm}^{-1}$  and C=O stretch at 1740–1880  $\text{cm}^{-1}$ ) groups. Carboxyl, anhydride,

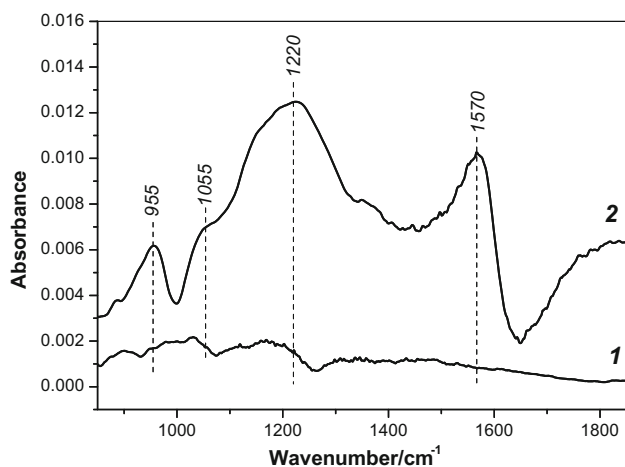
**Table 1** Pore structure parameters of the carbon supports

Sample	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1\text{a}}$	$V_{\text{p}}/\text{cm}^3 \text{ g}^{-1\text{b}}$	$D_{\text{av}}/\text{nm}^{\text{c}}$
CNT	196	1.49	30.3
CB	415	1.00	9.6

<sup>a</sup> BET specific surface area

<sup>b</sup> Total pore volume

<sup>c</sup> Average pore diameter calculated from the BET surface area and total pore volume as  $4V_{\text{p}}/S_{\text{BET}}$



**Fig. 2** FTIR absorption spectra of surface functional groups of CNT (1) and CB (2)

quinone, and lactone groups are acidic [24] and their presence explains the relatively low PZC value of CB. These groups decrease the hydrophobicity of the carbon, making the surface more accessible for the aqueous solution of the metal precursor. Phenols and ethers are weakly acidic or neutral. It has been found that these oxygen groups increase the interaction of the metal precursor with the support [24].

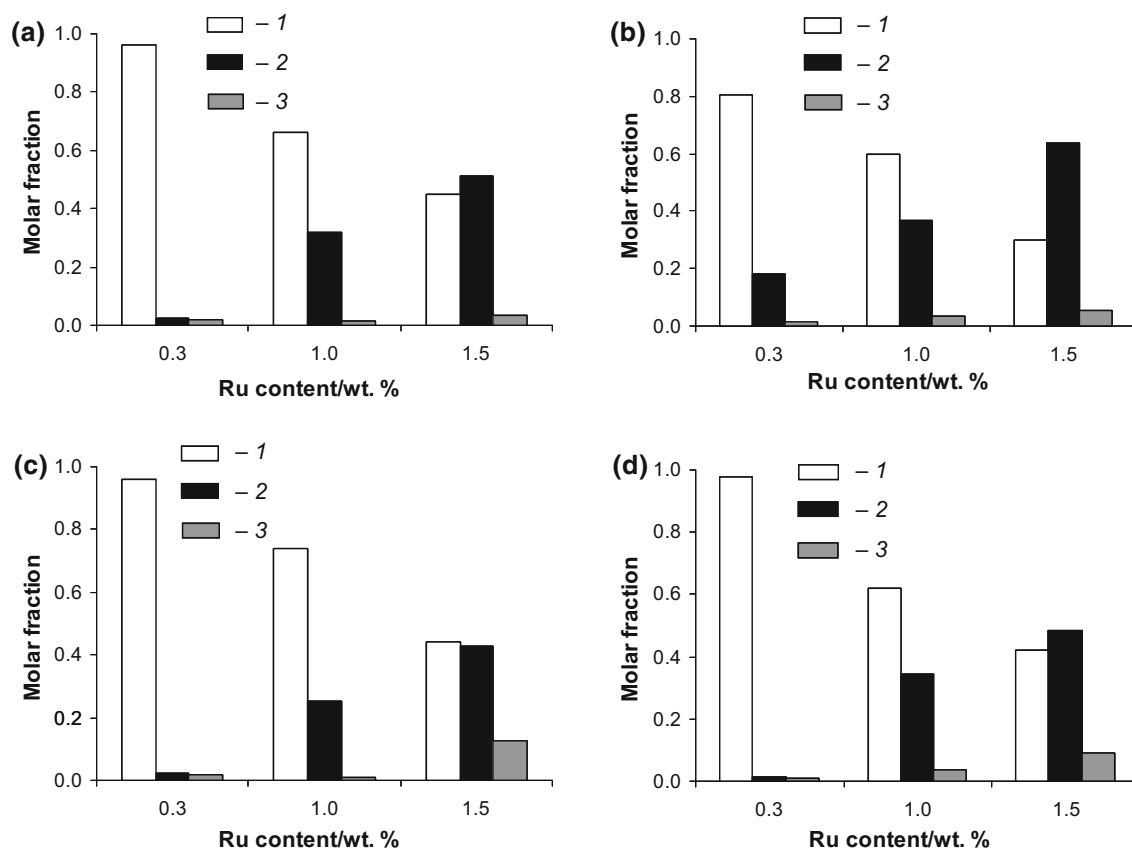
The Ru/CNT and Ru/CB catalysts with the metal content of 0.3, 1.0, and 1.5 wt% were tested in hydrogenation of benzaldehyde in ethanol medium at temperatures of 313 and 333 K and a hydrogen pressure of 0.5 MPa. Results of the catalytic measurements are displayed in Fig. 3 as composition of the reaction products vs. ruthenium content of the catalyst. It was shown that under the chosen reaction conditions, the presence of Ru/C samples did not provide a complete conversion of benzaldehyde. A maximum conversion of 71 % was attained when the reaction was performed at 333 K in the presence of 1.5 % Ru/CNT.

The reaction products consisted mainly of benzyl alcohol and much smaller amounts of benzaldehyde diethyl acetal (Scheme 1). The latter resulted from the interaction of benzaldehyde and ethanol with the involvement of acid sites of the support [10]. Somewhat higher amount of this by-product is observed for the Ru/CB catalysts (Fig. 3). A possible reason is that CB support has more acidic nature compared to CNT.

The catalytic hydrogenation of benzaldehyde is usually accompanied by the formation of toluene due to hydrogenolysis of the carbon–oxygen bonds in benzaldehyde and benzyl alcohol [8, 10, 11]. Moreover, it is known that ruthenium catalysts (e.g., Ru/C or Ru/Al<sub>2</sub>O<sub>3</sub>) are active in the hydrogenation of aromatic ring and thus may be non-selective for benzyl alcohol due to formation of cyclohexanecarboxaldehyde and cyclohexanemethanol [12, 34]. However, in the case of the catalysts under consideration, hydrodeoxygenation into toluene and hydrogenation of aromatic ring are completely suppressed irrespective of the reaction conditions and ruthenium content in the catalyst; thus, high selectivity for benzyl alcohol is maintained.

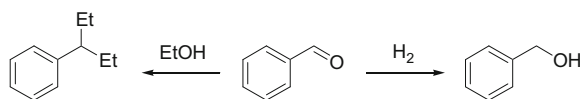
In general, a rise in the temperature from 313 to 333 K increases the conversion of benzaldehyde without significant change in selectivity for benzyl alcohol. Thus, for the Ru/CNT samples containing 1.0 and 1.5 % Ru, raising the temperature does not affect the benzyl alcohol selectivity, which remains at a high level (about 90 %).

As follows from the catalytic measurements (Fig. 3), the catalysts containing 0.3 % of ruthenium were low active in hydrogenation of benzaldehyde. 0.3 % Ru/CNT, being the most active sample among such catalysts, gave a molar fraction of benzyl alcohol equal to 0.18 (benzaldehyde conversion of 20 %). As ruthenium content of the samples was raised, this increased the fractions of both benzyl



**Fig. 3** Molar fractions of benzaldehyde (1) and its hydrogenation products [benzyl alcohol (2) and benzaldehyde diethyl acetal (3)] in ethanol medium in the presence of Ru/CNT (a, b) and Ru/CB (c, d) catalysts at 313 (a, c) and 333 K (b, d) during 4 h

#### Scheme 1



alcohol and by-product benzaldehyde diethyl acetal in the catalyze. At the same time, CNT catalysts were most active in the formation of benzyl alcohol. For example, due to hydrogenation of benzaldehyde in the presence of 1.5 % Ru/CNT sample at 333 K, the molar fraction of benzyl alcohol attained 0.64 (the selectivity of 87 %) 4 h after the onset of experiment. The using of the 1.5 % Ru/CB catalyst under the same conditions was less efficient: the fraction of benzyl alcohol was only 0.48 (the selectivity of 76 %). Thus, in terms of benzaldehyde conversion and benzyl alcohol selectivity, the investigated 1.5 % Ru/C catalysts are not inferior to some Ru systems prepared using complex composite supports [13–15].

The growth of benzaldehyde diethyl acetal amount with raising the ruthenium content of the samples may be caused by an increase in acidity of the support. Acidity of the support could increase because ruthenium was deposited

from the solutions containing chloride complexes. Due to transformation of such complexes on the surface of carbon supports, chloride ions leave the coordination sphere of ruthenium and modify the support surface.

It should be noted that properties of the Ru/CNT and Ru/CB catalysts substantially differ from those of palladium catalysts that were synthesized with the same supports and examined under the same conditions [30]. Although the palladium systems Pd/CNT and Pd/CB demonstrated a much higher activity, selectivity for benzyl alcohol was not high in some cases owing to the increased role of hydrodeoxygenation processes. Thus, in the presence of the 1.5 % Pd/CB catalyst, a complete conversion of benzaldehyde was already observed 1 h after the onset of experiment at 333 K, and toluene content in the catalyze reached 92 % (Table 2).

To elucidate the reasons of different hydrogenation activity of the Ru/CNT and Ru/CB catalysts, the formation of ruthenium sites was examined by temperature-programmed reduction (H<sub>2</sub>-TPR) and dispersions of metal particles were determined. The study was performed with the samples containing 1.5 % of ruthenium, which were most active in hydrogenation of benzaldehyde. The H<sub>2</sub>-TPR profiles of

**Table 2** Catalytic properties of Pd/C samples with different contents of palladium, as measured in hydrogenation of benzaldehyde in ethanol medium at 333 K and 0.5 MPa, 1 h after the onset of experiment

Catalyst	X/% <sup>a</sup>	Composition of the products/mol %			
		BA <sup>b</sup>	BEE <sup>c</sup>	BDA <sup>d</sup>	T <sup>e</sup>
0.3 % Pd/CNT	22	14.5	0.2	5.0	0
0.3 % Pd/CB	20	3.8	1.5	10.9	0
1.0 % Pd/CNT	95	89.2	1.6	2.8	0.9
1.0 % Pd/CB	95	78.0	10.2	0.8	5.5
1.5 % Pd/CNT	100	80.6	2.1	0.1	17.1
1.5 % Pd/CB	100	6.7	1.0	0	92.2

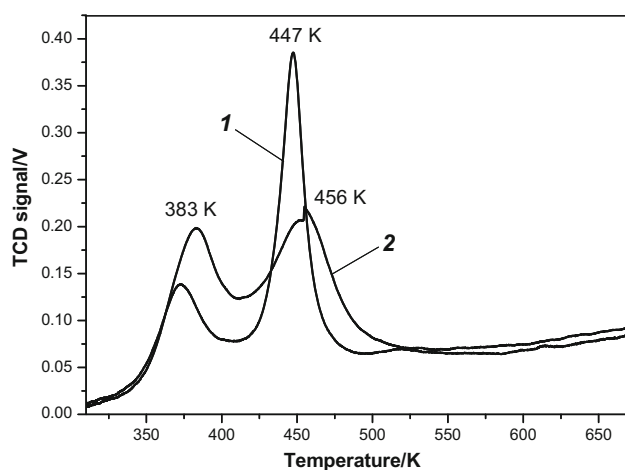
<sup>a</sup> Conversion of benzaldehyde calculated by Eq. (3)

<sup>b</sup> Benzyl alcohol

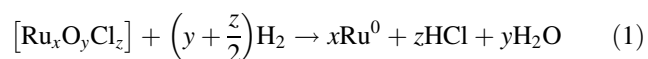
<sup>c</sup> Benzyl ethyl ether

<sup>d</sup> Benzaldehyde diethyl acetal

<sup>e</sup> Toluene

**Fig. 4** H<sub>2</sub>-TPR profiles of ruthenium chloride complexes deposited on the carbon supports: 1.5 % Ru/CNT (1) and 1.5 % Ru/CB (2). Prior to measurements, the samples were dried in air at room temperature

Ru/C samples have at least two hydrogen consumption regions (Fig. 4), which supposedly correspond to the reduction of supported species, differing either in the chemical composition (hydrolysis products) or in the strength of interaction with the support [35, 36]:



The reductions occur nearly identical in Ru/CNT and Ru/CB that may be due to proximity of the composition of surface complexes in the both samples. Decomposition and integration of H<sub>2</sub>-TPR signals allowed to evaluate the ratio of ruthenium species reduced at different temperatures. It was found that for the both samples, the relative contents of low- and high-temperature species are equal to 34 and

**Table 3** Dispersion of ruthenium in Ru/C samples and the calculated initial activities of the samples that were tested in hydrogenation of benzaldehyde at 313 and 333 K and 0.5 MPa

Catalyst	D/% <sup>a</sup>	d/nm <sup>b</sup>	d <sub>av</sub> /nm <sup>c</sup>	A/mol mol <sup>-1</sup> h <sup>-1d</sup>	
				313/K	333/K
1.5 % Ru/CNT	37	3.0	1.8	620	715
1.5 % Ru/CB	61	1.6	1.3	235	311

<sup>a</sup> Ruthenium dispersion estimated from O<sub>2</sub> chemisorption

<sup>b</sup> The size of ruthenium particles calculated from the dispersion values by a method reported in [40]

<sup>c</sup> The average size of ruthenium particles estimated by a STEM-HAADF

<sup>d</sup> Initial activity corresponding to the amount of benzaldehyde converted to benzyl alcohol on metallic sites with the known dispersion during 1 h after the onset of reaction

66 %, respectively. However, we can speculate that unlike the 1.5 % Ru/CNT sample, 1.5 % Ru/CB 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<sub>2</sub>-TPR peaks are shifted toward high temperatures (Fig. 4).

Estimation of the supported metal dispersion by oxygen chemisorption showed that the reduction of a precursor in the Ru/CNT sample leads to the formation of ruthenium particles with a lower dispersion compared to Ru/CB (Table 3).

As can be seen from STEM-HAADF images (Fig. 1), Ru/CB sample contains ruthenium particles with a denser location and better dispersion compared to Ru/CNT. The average particle sizes are determined to be around 1.8 and 1.3 nm for Ru/CNT and Ru/CB, respectively (Table 3), which is in agreement with O<sub>2</sub> chemisorption data. It is known that the particle size of supported metal is determined mostly by the texture of the support if the catalyst is prepared by incipient wetness impregnation. Therefore, highly dispersed particles of ruthenium were formed on the support with a more developed pore structure, i.e., on CB (see Table 1). However, the size of ruthenium particles calculated from chemisorption is somewhat higher than that estimated from microscopic study. A possible reason is that O/Ru stoichiometry assumed for calculation of metal dispersion may be less than 1 (e.g., 0.75 [37]). Besides, the high-temperature pre-reduction can lead to a partial coverage of Ru particles by the support as has been shown for various carbon-supported noble metal catalysts [38]. This encapsulation could also account for the lower chemisorption uptake than would be expected based on the microscopic measurements.

As follows from the comparison of calculated initial activities (Table 3), the activity of 1.5 % Ru/CNT catalyst



in the formation of benzyl alcohol is more than twofold higher compared to 1.5 % Ru/CB. Hydrogenation of benzaldehyde is known to be a structure-sensitive reaction [11]: the catalytic activity improves with increasing the size of metal particles. Thus, differences in hydrogenation activity of the studied samples can be attributed to the effect of support (pore structure, morphology, and chemical composition of functional cover) on the dispersion of supported metal. Nevertheless, it cannot be excluded that electronic state of ruthenium particles supported on CNT and CB may vary and influence hydrogenation activity of the catalysts studied.

## Conclusions

The present study has demonstrated that hydrogenation of benzaldehyde in ethanol medium in the presence of Ru/C catalysts occurs selectively with the preferential formation of benzyl alcohol without subsequent hydrodeoxygenation into toluene. An increase in ruthenium content of the catalysts improves their activity at a high selectivity for benzyl alcohol. The Ru/CB catalysts with highly dispersed ruthenium showed a much lower activity in hydrogenation of benzaldehyde to benzyl alcohol compared to Ru/CNT samples.

## Experimental

### *Catalyst preparation and characterization*

Multi-wall CNT Baytubes<sup>®</sup> C 150 HP were purchased from Bayer MaterialScience AG (Leverkusen, Germany), and CB P278-E (analog to N472) was supplied by Experimental Technology Department of Institute of Hydrocarbons Processing (Omsk, Russia). Prior to experiments, carbon supports were dried overnight in air at 393 K to remove the adsorbed water.

Nitrogen adsorption–desorption data of the supports were obtained with an ASAP-2020 (Micromeritics) volumetric vacuum static unit at 77 K. Before the measurements, samples were degassed for 10 h at 523 K. The Brunauer–Emmett–Teller specific surface area ( $S_{\text{BET}}$ ) was obtained from the adsorption isotherm in the range of equilibrium relative pressures of nitrogen  $P/P_0 = 0.05$ – $0.25$ . The total pore volumes ( $V_p$ ) were determined from the nitrogen adsorption at  $P/P_0 = 0.99$ , assuming the adsorbate density equal to that of normal liquid,  $0.02887 \text{ mol cm}^{-3}$ . The PSD curves were obtained from desorption branches of isotherms using the Barrett–Joyner–Halenda method.

The composition of surface functional groups of CNT and CB was studied using FTIR spectroscopy on a Nicolet-5700 (Thermo Fisher Scientific) instrument. Thin carbon

films prepared by deposition of CNT or CB on BaF<sub>2</sub> glasses were used as the samples for FTIR spectroscopy [31]. FTIR spectra were recorded in a transmission mode over the range of 850–2000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The assignment of absorption bands was made taking into account the data published in [31–33].

A preliminary study of the adsorption of ruthenium(IV) chloride complexes demonstrated a very low adsorptivity of CNT and CB. A maximum amount of ruthenium anchored on these supports by chemisorption did not exceed 0.28 wt%. So, samples of supported catalysts with the metal contents of 0.3, 1.0, and 1.5 wt% were obtained by incipient wetness impregnation of the carbon supports with aqueous solutions of ruthenium(IV) chloride complexes. The impregnating solutions with a specified concentration of precursor were prepared using ruthenium(IV) hydroxytrichloride (pure grade, JSC “Aurat”) dissolved in concentrated hydrochloric acid (the Ru to HCl molar ratio of 1:3). Ruthenium content in the solutions was estimated by optical emission spectrometry with inductively coupled plasma on a Varian 710-ES spectrometer.

After deposition of the precursor on the supports and drying in air at room temperature, the Ru-containing samples were examined by H<sub>2</sub>-TPR using an AutoChem II 2920 (Micromeritics) chemisorption analyzer with a thermal conductivity detector. The H<sub>2</sub>-TPR experiments were carried out with a mixture of 10 % H<sub>2</sub> and argon (the flow rate of 25  $\text{cm}^3 \text{ min}^{-1}$ ) in a temperature range of 308–673 K at a heating rate of 10  $\text{K min}^{-1}$ .

The dispersion of ruthenium in the Ru/C samples was estimated by pulse chemisorption of oxygen after reduction to 523 K and cooling the sample in an inert gas to the temperature of experiment (273 K). The 10 % O<sub>2</sub>–He mixture was fed into the flow of inert carrier gas by pulses at equal time intervals. The process was run until the detector signal became constant. The metal dispersion was calculated taking into account the adsorption stoichiometry O/Ru = 1 [39]. The size of the ruthenium particles was calculated using the expression:

$$d = 3.32d_{\text{Ru}}D^{-1.23}, D > 0.2, \quad (2)$$

where  $d$  is the size of metal particles,  $d_{\text{Ru}}$  is the atomic diameter of ruthenium (0.269 nm), and  $D$  is the dispersion estimated from the chemisorption. This equation has been derived for a close-packed metal structure, under the assumption that the crystallites form cubooctahedra or icosahedra [40].

STEM-HAADF images were taken by a JEM-2200FS (JEOL) instrument at 200 kV. The samples for the STEM-HAADF study were prepared on a perforated carbon film mounted on a copper grid. Approximately 50 ruthenium particles were measured for estimation of an average particle size ( $d_{\text{av}}$ ).

## Catalytic measurements

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

Liquid-phase hydrogenation of benzaldehyde (98 %, Acros Organics) in the presence of synthesized catalysts was studied using a 180 cm<sup>3</sup> steel autoclave. A 0.5-g catalyst sample was placed in the autoclave with 30 cm<sup>3</sup> of ethanol (96 %). 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 using the 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<sup>3</sup> of benzaldehyde and 65 cm<sup>3</sup> of ethanol were loaded into the autoclave. The hydrogenation was performed for 5 h at 313 and 333 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 GC–MS (Agilent 5973 N/6890 N). The quantitative determination of the reaction products was carried out every hour by GC (Hewlett Packard 5890 Series II) in a capillary column HP-PONA (50 m × 0.20 mm, Agilent Technologies) with linear heating from 313 to 473 K during analysis.

Benzaldehyde conversion  $X$  (%) and benzyl alcohol selectivity  $S$  (%) were determined as follows:

$$X = \frac{C_{B,0} - C_B}{C_{B,0}} \times 100 \quad (3)$$

$$S = \frac{C_{BA}}{X} \times 100, \quad (4)$$

where  $C_{B,0}$ ,  $C_B$ , and  $C_{BA}$  are the concentrations (wt%) of benzaldehyde before the reaction, benzaldehyde after the reaction, and benzyl alcohol, respectively.

Initial activities of the catalysts (1 h after the onset of reaction) were calculated from benzaldehyde conversions taking into account the dispersion of ruthenium estimated by pulse chemisorption.

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