Palladium–Ruthenium Catalyst for Selective Hydrogenation of Furfural to Cyclopentanol¹

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Abstract—Bimetallic Pd–Ru/C catalyst was shown to be much more active in the aqueous-phase hydrogenation of furfural (473 K, 8 MPa) in comparison with both Pd/C and Ru/C catalysts. The enhanced hydrogenation activity manifested itself as an increased yield of cyclopentanol (77%) at a complete conversion of furfural. The observed synergistic effect between palladium and ruthenium in the tested reaction can be related to changes in the electronic state and particle size of supported metals upon interaction with each other and the Pd–Ru alloy formation.

Keywords: furfural, selective hydrogenation, cyclopentanol, supported Pd-Ru catalysts, synergistic effect

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The catalytic processing of biomass-derived compounds has recently attracted much attention due to the possibility of obtaining valuable chemical products from renewable raw materials [1-3]. Furfural is an important platform compound produced commercially from plant polysaccharides. The catalytic hydrogenation of furfural yields a wide range of useful intermediates [4–11]. By now, various supported catalysts containing noble metals have been proposed to perform this reaction with the selective obtaining of furfuryl alcohol (FA) [5, 7, 8], 2-methylfuran (MF) [5, 9], tetrahydrofurfuryl alcohol (THFA) [5, 10], 1,2-pentanediol (PDL) [11] and 1,5-pentanediol [10].

Currently, the using of water as reaction medium in furfural hydrogenation is attractive and preferable for the following reasons. Firstly, water is non-toxic and inexpensive solvent. It is important from the viewpoint of environmental and green chemistry [12]. Secondly, furfural is obtained in industry as aqueous solutions [13]. Thus, costly separation of furfural—water can be

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obviated if the hydrogenation is performed in water medium. Finally, water may be involved in the catalytic transformations during the hydrogenation of furfural. This enables to obtain a large number of valuable chemicals [14-22].

Previously [14–16], it has been found that the aqueous-phase hydrogenation of furfural over Pt/C, Pd/C and Ru/C catalysts at temperatures more than 413 K and pressures above 3 MPa is accompanied by a Piancatelli-type rearrangement with participation of water as nucleophile (Scheme 1).

The subsequent hydrogenation of rearrangement product allowed obtaining cyclopentanone (CPN) with a high yield (up to 76.5%) [14, 16]. Among the by-products, THFA and 2-methyltetrahydrofuran (MTHF) have been detected. However, further hydrogenation of CPN to cyclopentanol (CPL) is suppressed, which is caused by blocking of catalytically active sites by the products of polycondensation of FA [15].



Scheme 1. Reaction pathways of furfural hydrogenation in aqueous medium.

In order to retain or even improve the catalytic activity and stability to deactivation, the second metal can be introduced into the supported catalyst [23–29]. Among numerous bimetallic catalysts, the palladium-ruthenium composites have attracted attention due to their much improved or novel catalytic properties [28]. Very recently, we have found that bimetallic Pd–Ru/C catalysts are much more active in the liquid-phase hydrogenation of benzaldehyde than the Pd/C and Ru/C monometallic catalysts [29]. Depending on the nature of carbon supports, Pd–Ru/C catalysts allow significant increase in the yield of benzyl alcohol or toluene at a complete conversion of benzaldehyde.

The present work deals with the study of supported palladium, ruthenium and palladium—ruthenium catalysts based on carbon nanotubes (CNTs) in the aqueous-phase hydrogenation of furfural. The choice of carbon support was caused by high activity of Pd— Ru/CNTs catalyst in liquid-phase hydrogenation of benzaldehyde [29]. Moreover, there are other reasons for choice of CNTs as the support, namely: a developed system of mesopores is to be favorable for using in liquid-phase catalytic processes, a relatively low content of oxygen functional groups on the surface obstructs the side acid—base reactions [30, 31]. It should be noted that due to their physicochemical characteristics, CNTs are widely used as the support of highly effective hydrogenation catalysts [32, 33].

EXPERIMENTAL

Materials and Reagents

The multi-wall CNTs Baytubes[®] C 150 HP (Bayer Material Science AG, Germany) were used as the support. Physicochemical properties of CNTs were studied in previous works [30, 34]. PdCl₂ and Ru(OH)Cl₃

(both >98%, Aurat, Russia) were used for catalyst preparation without further purification. Furfural (99%, Sigma-Aldrich) was purified by distillation before use. For qualitative analysis of reaction mixtures, the authentic samples of MF (99%, Carl Roth), THFA (99%, Sigma-Aldrich), MTHF (99%, Acros Organics), CPN (99%, Sigma-Aldrich), CPL (99%, Sigma-Aldrich), 1-butanol (>98%, Reakhim), 2-pentanol (98%, Sigma-Aldrich), 1-pentanol (>98%, Acros Organics), PDL (96%, Acros Organics), tetrahydrofuran (>98%, Reakhim) were used. Hydrogen gas (99.99%, Novosibirsk Chemical Concentrates Plant, Russia) was used for reduction of the catalysts and the catalytic hydrogenation.

Catalyst Preparation

Before the preparation of the catalysts, the carbon support was dried overnight in air at 393 K to remove the adsorbed water. The catalysts were obtained by incipient wetness impregnation of CNTs with the solutions of chloride precursors as described elsewhere [29, 30, 34]. The content of palladium and ruthenium in monometallic catalysts was 1.5 wt %. Bimetallic catalyst contained 0.85 wt % Pd and 0.80 wt % Ru (the Pd : Ru molar ratio of 1.0). After the impregnation, the samples were dried in air at room temperature. Before characterization and catalytic experiments, the catalysts were additionally dried in argon flow at 423 K for 0.5 h and then reduced in flowing hydrogen at 523 K for 2 h.

Catalyst Characterization

Palladium and ruthenium contents in the catalysts were estimated by atomic emission spectrometry with inductively coupled plasma on a Varian 710-ES spectrometer (Agilent Technologies, United States) after complete dissolution of the samples in a mixture of

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n determination) ratio of 1.0 wa

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nitric and perchloric acids (palladium determination) or nitric and hydrochloric acids (ruthenium determination).

High resolution transmission electron microscopy (HRTEM) images of the catalysts were taken by a JEM-2100 (JEOL, Japan) instrument with the grating resolution of 0.14 nm at the 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 (EDX) analysis was performed with an INCA 250 (Oxford Instruments, Great Britain) spectrometer.

X-ray photoelectron spectroscopy (XPS) measurements of the catalysts were carried out on a SPECS (SPECS Surface Nano Analysis, Germany) spectrometer at a residual pressure of 7×10^{-7} Pa in the analyzer chamber. To avoid oxidation of supported metals, contact with air of the pre-reduced samples was minimized. The spectra were recorded using monochromatic Al K_{α} radiation (hv = 1486.7 eV). Preliminarily, the binding energy scale of the spectrometer was calibrated against signals obtained from metallic gold and copper, Au4 $f_{7/2}$ (84.0 eV) and Cu2 $p_{3/2}$ (932.6 eV). The spectra were calibrated with respect to C1s line of the carbon support (284.6 eV).

Catalytic Experiments and Analysis of Reaction Products

The hydrogenation of furfural in the presence of the synthesized catalysts was performed in a limbo li (Büchi AG, Switzerland) periodic reactor. A catalyst sample (500 mg) was placed into the autoclave with water (95 cm³) and furfural (5.0 cm^3). Then, the autoclave was purged by argon and filled by hydrogen. The hydrogenation was carried out for 3 h at a temperature of 473 K and a total pressure of 8 MPa under vigorous stirring (1500 min⁻¹) of the reaction mixture. Sampling from the reactor (1 cm³) was performed every 0.5 h.

The reaction products were identified by ¹³C NMR spectroscopy. The spectra were recorded on an Avance-400 (Bruker, United States) spectrometer at the Larmor frequency of 100.6 MHz using *J*-modulated pulse sequence [35]. The quantitative composition of the reaction mixtures was determined 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.

RESULTS AND DISCUSSION

Pd-Ru/CNTs catalyst with the total content of supported metals of 1.65 wt % and the Pd : Ru molar

ratio of 1.0 was tested in the aqueous-phase hydrogenation of furfural at a temperature of 473 K and total pressure of 8 MPa. Results of the catalytic measurements were compared with the data obtained under identical conditions for monometallic 1.5%Pd/CNTs and 1.5%Ru/CNTs catalysts. The identification of reaction products was carried out by ¹³C NMR spectroscopy. Analysis of ¹³C NMR spectra allowed to establish the presence of THFA, MTHF and CPL in the reaction mixtures. The qualitative composition of the mixtures of products was confirmed by GC analysis with comparison of the retention times using authentic samples. Thus, MF, CPN, PDL, 2-pentanol, 1-pentanol, 1-butanol, furan and tetrahydrofuran were additionally detected. The analysis revealed no traces of FA and intermediates of its conversion to CPN (4-hydroxy-2-cyclopentenone, 2-cyclopentenone). Despite this, based on literature data as well as analysis of reaction products, it is reasonable to suggest that the conversion during the aqueous-phase hydrogenation of furfural over the catalysts proceeds according to the above scheme.

In the presence of Pd-Ru/CNTs catalyst, a complete conversion of furfural is achieved already after 1 h of the reaction and CPL predominates among the products (Fig. 1a). Further hydrogenation of CPN leads to increase in the selectivity for CPL up to about 77% (Table 1). In the presence of monometallic Pd/CNTs catalyst, a complete conversion of furfural is also achieved. However, the yield of CPL is only about 14% even after 3 h of the reaction and CPN prevails among the products (Fig. 1b, Table 1). The ruthenium catalyst is even less active compared to Pd/CNTs and Pd-Ru/CNTs samples. In the presence of this catalyst, a full conversion of furfural with the formation mainly of CPN (selectivity up to 51%) is achieved only at the end of the experiment (Fig. 1c, Table 1). It is interesting to note that, unlike Pd and Pd-Ru samples, the main route of furfural transformation over Ru/CNTs catalyst at the beginning of the reaction is decarbonylation to furan. During the experiment, the selectivity for furan decreases from 41 to 10% due to the parallel reduction reactions of furfural to other products (Fig. 1c).

As has been mentioned above, the aqueous-phase hydrogenation of furfural over noble metal-based catalysts allows obtaining CPN with a high selectivity, whereas further reduction to CPL is suppressed [14–16]. A comprehensive search on published sources showed that 5%Ru/C catalyst, which is most active in the target reaction (among the other supported catalysts based on noble metals), allows producing CPL with relatively low selectivity (up to 47%) [5].



Fig. 1. Furfural conversion $(1, \blacksquare)$ and selectivities for THFA $(2, \bullet)$, CPN $(3, \bigcirc)$, MTHF $(4, \bullet)$, CPL $(5, \diamondsuit)$ and furan $(6, \blacktriangle)$ vs. time during aqueous-phase hydrogenation over catalysts Pd–Ru/CNTs (a), Pd/CNTs (b) and Ru/CNTs (c) at a temperature of 473 K and pressure of 8 MPa.

It is interesting that the yield of the products of FA hydrogenation (predominantly, THFA and MTHF) was low, independently of the catalyst used. In all cases, the reaction route involving water prevails. Apparently, this is due to such reaction conditions (473 K, 8 MPa), which are favorable to involve water in the furan ring rearrangement. Under much milder conditions (<363 K, <2 MPa), water does not participate in transformations and the aqueous-phase furfural hydrogenation yields mainly FA and THFA [30, 34].

Thus, bimetallic Pd–Ru/CNTs catalyst exhibits superior performance in the aqueous-phase hydrogenation of furfural to CPL compared to monometallic Pd/CNTs and Ru/CNTs catalysts. Under the chosen reaction conditions (473 K, 8 MPa), the bimetallic catalyst allows achieving a high selectivity for CPL (up to about 77%) at a complete conversion of furfural.

In order to elucidate the reasons for the observed differences in the catalytic properties, the samples were investigated by XPS and HRTEM. XPS was used to estimate the oxidation state of supported metals. The XPS data can indicate the interaction between palladium and ruthenium in bimetallic catalyst. The $Pd3d_{5/2}$ and $Pd3d_{3/2}$ spectra recorded for Pd/CNTs and Pd-Ru/CNTs catalysts can be decomposed into two overlapping peaks, which indicates that supported palladium has two electronic states (Fig. 2a). The positions of the signals with lower binding energy values $(3d_{5/2}$ region) are close to those observed for metallic palladium (335.7 \pm 0.3 eV [36, 37]), whereas the signals with higher values of binding energy can be attributed to the electron-deficient palladium species $Pd^{\delta+}$ (337.9 ± 0.3 eV for PdCl₂ [36, 37]). To estimate the oxidation state of ruthenium in the Ru/CNTs and

Catalyst	x, %**	<i>S</i> , %**						
		THFA	CPN	MTHF	CPL	furan	other products***	
Pd/CNTs	100	10.3	36.2	17.9	14.1	0.1	21.4	
Pd-Ru/CNTs	100	7.0	0.8	4.5	76.8	1.9	9.0	
Ru/CNTs	100	4.8	51.3	1.1	18.4	10.2	14.2	

Table 1. Catalytic properties of Pd/CNTs, Ru/CNTs and Pd-Ru/CNTs samples in the aqueous-phase hydrogenation of furfural*

* Reaction conditions: 95 cm³ of water, 5.0 cm³ of furfural, 500 mg of catalyst, T = 473 K, P = 8 MPa, duration of 3 h.

** x is the conversion of furfural according to GC, S is the selectivity of products formation according to GC.

*** Among the other products, MF, PDL, 2-pentanol, 1-pentanol, 1-butanol and tetrahydrofuran were detected by NMR and GC.

Pd-Ru/CNTs samples (Fig. 2b), the Ru $3p_{3/2}$ peak was employed, since the signals from ruthenium in the Ru3d region overlap with the C1*s* line from the support [38, 39].

As follows from the analysis of spectra, a notable shift of the maxima of Pd^0 and $Pd^{\delta+}$ lines toward high binding energy values and a decrease in the Pd^0 : $Pd^{\delta+}$ atomic ratio are observed for Pd-Ru/CNTs with respect to Pd/CNTs catalyst (Fig. 2a, Table 2). At the same time, a negative shift of $Ru3p_{3/2}$ peak occurs for Pd-Ru/CNTs sample with respect to monometallic Ru/CNTs catalyst (Fig. 2b, Table 2). The Ru $3p_{3/2}$ signal in the spectrum of bimetallic sample can be assigned to metallic ruthenium. Such changes in the oxidation state of supported palladium and ruthenium in bimetallic Pd-Ru system have been found earlier [29, 40, 41] and can be caused by the interaction of metals with each other during the formation of Pd-Ru alloy. The direction of electron transfer (from palladium to ruthenium) is possibly related to a greater surface electronegativity of ruthenium in comparison with palladium [42].

The formation of Pd–Ru bimetallic nanoparticles was confirmed by HRTEM with EDX analysis of reduced Pd–Ru/CNTs catalyst. As shown in one of the HRTEM images (Fig. 3b), this sample has nanoparticles with a *d*-spacing of 0.217 nm, which does not correspond to any lattice spacings of Pd or Ru and very close to that of the (111) facet of face-centered cubic lattice for Pd–Ru alloy (0.219 nm [28, 43]). The EDX spectrum (Fig. 3c) recorded from the region emphasized in Fig. 3b includes signals corresponding to Pd and Ru. This confirms that supported nanoparticles in Pd–Ru/CNTs catalyst are bimetallic.

As shown by a comparison of HRTEM data for the Pd/CNTs, Ru/CNTs and Pd–Ru/CNTs catalysts, the dispersion of nanoparticles in bimetallic sample is noticeably higher than that in the corresponding monometallic systems. The bimetallic nanoparticles have a spherical shape and the average size is equal to 1.6 nm (Fig. 3d), whereas the palladium and ruthenium nanoparticles in corresponding monometallic



Fig. 2. Pd3d (a) and Ru3p (b) spectra of Pd/CNTs, Pd-Ru/CNTs and Ru/CNTs catalysts.

catalysts have the average size of 2.3 and 1.8 nm, respectively. A decrease in size of nanoparticles upon Pd–Ru alloy formation is in agreement with CO chemisorption data obtained earlier [29, 30].

Catalvet	Binding energy	y of Pd3 $d_{5/2}$, eV	Binding energy	$Pd^0: Pd^{\delta+}$ atomic ratio	
Catalyst	Pd^0	$Pd^{\delta +}$	of $\operatorname{Ru}3p_{3/2}$, eV		
Pd/CNTs	336.2	337.9	_	1.0	
Pd-Ru/CNTs	336.4	338.2	462.2	0.7	
Ru/CNTs	_	_	462.5	_	

Table 2. Results of XPS analysis of Pd/CNTs, Ru/CNTs and Pd-Ru/CNTs catalysts







(c)







Thus, an increased activity of bimetallic Pd-Ru/CNTs catalyst in the aqueous-phase hydrogenation of furfural can be caused by the mutual interaction of supported Pd and Ru, which increases the dispersion of nanoparticles and changes the electronic state of metals. A decrease in size of metal nanoparticles increases the fraction of active sites accessible to reactants. A change in electronic state can promote the activation of hydrogen and substrate molecules. In viewpoint of the electronic factor, it is difficult to unequivocally establish a participation of palladium and ruthenium species as active sites in the 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 [44, 45]. In this case, the promotion effect is due to the presence of electron-deficient metal species which enhance the polarization of C=O bond of furfural as well as CPN formed during the reaction (Fig. 4). The electron transfer from Pd to Ru 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 molecules of carbonyl compounds. As a result of electrophilic activation, the C=O bond is weakened, thus facilitating a subsequent addition of chemisorbed hydrogen [46]. Moreover, due to electron transfer from palladium to ruthenium, the latter is present in the Pd-Ru/CNTs catalyst as Ru⁰. 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 [47]. So, the preferential sites of H_2 adsorption and activation are represented most likely by the electronrich supported ruthenium species.

CONCLUSIONS

In summary, we found that bimetallic Pd–Ru catalyst based on carbon nanotubes exhibits superior performance in the aqueous-phase hydrogenation of furfural to cyclopentanol compared to monometallic palladium and ruthenium catalysts prepared by using the same support. Under the chosen reaction conditions (473 K, 8 MPa), the bimetallic catalyst allows achieving selectivity for cyclopentanol up to about 77% at a complete conversion of furfural. The data obtained for the catalysts by HRTEM and XPS suggest that an increased hydrogenation activity of bimetallic sample 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

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Fig. 4. Supposed modes of adsorption and activation of furfural and CPN molecules on the surface of Pd-Ru nanoparticles.

observed synergistic effect between palladium and ruthenium can be caused by facilitation of electrophilic activation of the C=O bonds in furfural and intermediate cyclopentanone owing to an increased fraction of electron-deficient palladium species.

The obtained result may be useful for the development of efficient catalysts for the hydrogenation of furfural to cyclopentanol, which is a starting compound in the synthesis of pharmaceuticals, fragrances, fungicides [17, 18, 48]. Conventionally, cyclopentanol is produced by oxidation of cyclopentene or cyclization of 1,6-hexanediol with subsequent reduction of cyclopentanone. At the same time, the aqueous-phase hydrogenation of furfural can be regarded as one-pot synthesis of cyclopentanol from a renewable source.

Further research will focus on optimizing the composition of the catalyst (a carbon support, content and ratios of supported metals) and the reaction conditions allowing to receive cyclopentanol with the most selectivity.

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