

Selective aqueous-phase hydrogenation of furfural to cyclopentanol over PdRu/C catalyst*

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The bimetallic PdRu catalyst supported on carbon nanotubes were found to provide an efficient synthesis of cyclopentanol in aqueous-phase hydrogenation of furfural. Under the chosen reaction conditions (temperature of 473 K, total pressure of 8 MPa), the selectivity towards cyclopentanol reaches 77% at a complete conversion of furfural. A high activity of this catalyst can be associated with changes in the electronic state and dispersion of the supported metals caused by their mutual interaction and formation of PdRu alloy.

Key words: furfural, catalytic hydrogenation, bimetallic catalyst, cyclopentanol.

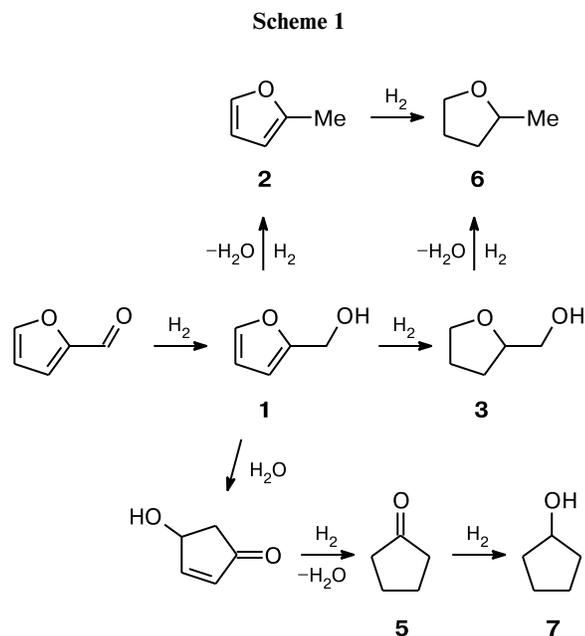
Catalytic hydrogenation of furfural, large scale product of biomass processing, makes it possible to produce a wide range of valuable chemicals based on renewable sources.^{1–3} In the present time, a variety of supported catalysts with different composition were proposed for liquid-phase hydrogenation of furfural, in particular, the catalysts based on noble metals. They demonstrate high activity in this reaction enabling the synthesis of furfuryl alcohol (**1**)^{3,4}, 2-methylfuran (**2**)^{3,5}, tetrahydrofurfuryl alcohol (**3**)^{3,6}, 1,2-pentanediol (**4**)⁷, 1,5-pentanediol.⁶ When hydrogenation is carried out in aqueous solution, maintenance of stability of the catalyst becomes a challenge. The fact is that under the hydrothermal conditions of the reaction a loss in activity may occur due to phase transformations of the support or leaching of the active component.^{8,9} However, utilization of water as cheap and nontoxic solvent is preferable. Firstly, its usage corresponds to the concepts of green chemistry and is beneficial in terms of economic considerations.¹⁰ Secondly, the presence of water is favorable for obtaining a great number of important organic compounds since water participates in

catalytic conversions of substrate and intermediate products of hydrogenation.^{11–15}

It was shown earlier^{11,12} that aqueous-phase hydrogenation of furfural over Pt/C, Pd/C, and Ru/C catalysts at temperatures over 413 K and pressures over 3 MPa is accompanied by Piancatelli rearrangement. In this case, the rearrangement occurs with water acting as a nucleophilic agent (Scheme 1). Further hydrogenation of the product of rearrangement gives cyclopentanone (**5**) with a high yield (up to 76.5%).^{11,12} Among the by-products, alcohol **3** and 2-methyltetrahydrofuran (**6**) were detected, formation of which occurs *via* hydrogenation of the furan ring of alcohol **1**. Along with that, the subsequent hydrogenation of ketone **5** to cyclopentanol (**7**) appears to be hampered due to the poisoning of active sites with the products of polycondensation of alcohol **1**.¹⁶

Alcohol **7** is a valuable product applied as a solvent or a starting compound for the synthesis of drugs, flavors, and fungicides.^{13,14,17} Traditionally, it is produced by oxidation of cyclopentene or cyclization of 1,6-hexanediol followed by reduction of ketone **5**. At the present time, much attention of the researchers has been focused on search and study of supported metal catalysts which are active in aqueous-phase selective hydrogenation of furfural into alcohol **7**.^{3,13–15}

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Recently,¹⁸ we found that bimetallic PdRu/C catalysts were much more active in hydrogenation of benzaldehyde than monometallic Pd/C and Ru/C catalysts. Depending on the nature of carbon support of the bimetallic catalyst, the yield of benzyl alcohol (up to 90%) or toluene (up to 56%) significantly increases at overall conversion of benzaldehyde.

In the present work, a possibility of synthesis of alcohol **7** *via* aqueous-phase hydrogenation of furfural over Pd–Ru catalyst supported on carbon nanotubes (CNTs) has been studied. A choice of the catalyst is accounted for not only by high catalytic activity in the earlier studied reaction,¹⁸ but an enhanced stability of Pd–Ru system under conditions of liquid-phase hydrogenation.¹⁹ In addition, CNTs possess many advantageous characteristics, such as a well developed system of mesopores and relatively low content of oxygen-containing functional groups on its surface. Due to these properties this material is widely applied as a support for highly efficient catalysts for hydrogenation.^{20,21}

Experimental

Multiwall CNTs Baytubes C 150 HP (Bayer MaterialScience AG) were used as a support for the catalysts. The BET specific surface area was 196 m² g⁻¹, total pore volume was 1.49 cm³ g⁻¹, and the average pore diameter was 30.3 nm. The catalyst with the total content of Pd and Ru of 1.5 wt.% was prepared by the incipient wetness impregnation of CNTs with aqueous solution of chloride complexes of Pd^{II} and Ru^{IV}.¹⁸ The Pd : Ru molar ratio in the catalyst was 1. Pretreatment of the sample prior to the catalytic experiment included reduction under hydrogen flow at 523 K for 2 h.

Hydrogenation of furfural (99%, Sigma–Aldrich) in aqueous solution (3.5 wt.%, 100 mL) in the presence of PdRu/CNTs

(300 mg) was carried out in a periodic mode in a Limbo Li autoclave (Büchi AG) at a temperature of 473 K and overall pressure of 8 MPa with continuous stirring of the reaction mixture (1500 min⁻¹). The duration of any experiment was 3 h.

The products of hydrogenation were identified by ¹H and ¹³C NMR spectroscopy on an Avance-400 instrument (Bruker), at Larmor frequencies of 400 (¹H) or 100 MHz (¹³C). ¹³C NMR spectrum was recorded in a *J*-modulation regime (JMOD)²² which allows us to discriminate with carbon atoms which differ accordingly to a magnitude of ¹H–¹³C interaction. A quantitative composition of reaction mixtures, which were sampled every 0.5 h, was determined by GLC on a Hewlett–Packard 5890 Series II instrument equipped with capillar HP-1 column (100 m × 0.25 mm, Agilent Technologies) and flame-ionization detector.

Results and Discussion

At a temperature of 473 K and a pressure of 8 MPa the aqueous-phase hydrogenation of furfural for 3 h in the presence of PdRu/CNTs catalyst gave a mixture of products which were identified by NMR and GLC. The ¹H NMR spectrum of the reaction mixture contains signals corresponding only to nonaromatic protons. However, the reliable interpretation of the spectral data seems unfeasible due to numerous overlapping multiplet signals. The analysis of ¹³C NMR spectrum (Fig. 1) served to detect the compounds **3**, **6**, and **7** in the reaction mixture. Assignment of the signals as well as comparison of the obtained results with the published data are presented in Table 1. The qualitative composition of the reaction mixture was confirmed chromatographically by comparing the retention times of the components with those of the individual compounds. Additionally, the presence of the compounds **2**, **4**, **5**, as well as 2-pentanol, 1-pentanol, furan, 1-butanol and THF was established. We failed to detect any traces of alcohol **1** and intermediate products of its

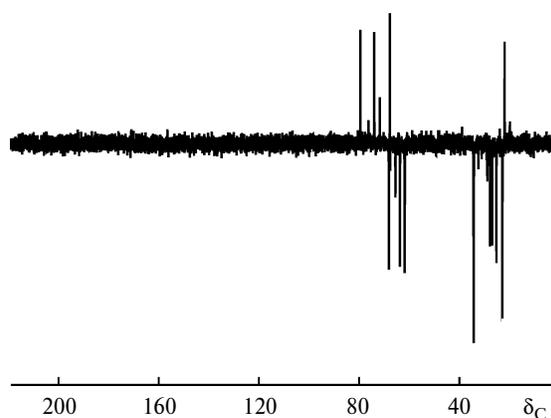


Fig. 1. ¹³C{¹H} NMR spectrum (JMOD) of the reaction mixture obtained in aqueous-phase hydrogenation of furfural over PdRu/CNTs catalyst for 3 h at a temperature of 473 K and a pressure of 8 MPa.

Table 1. Assignment of the signals of $^{13}\text{C}\{^1\text{H}\}$ NMR (JMOD) spectrum of the reaction mixture obtained at aqueous-phase hydrogenation of furfural over PdRu/CNTs at a temperature of 473 K and pressure of 8 MPa for 3 h

Compound	^{13}C NMR spectrum (δ_{C})	
	Experiment	Literature data
3	25.2 (C(4)), 26.9 (C(3)), 63.7 (CH ₂ OH), 68.1 (C(5)), 79.6 (C(2))	25.2, 27.4, 63.7, 67.2, 79.2 ^a
6	22.0 (CH ₃), 27.7 (C(4)), 34.4 (C(3)), 65.6 (C(5)), 76.3 (C(2))	21.02, 26.05, 33.29, 67.77, 75.34 ^b
7	22.8 (C(3), C(4)), 34.3 (C(2), C(5)), 74.0 (C(1))	23.2, 35.5, 74.0 ^c

^a See Ref. 23, solvent: DMSO-*d*₆.

^b See Ref. 24, solvent: CDCl₃.

^c See Ref. 25, solvent: CDCl₃.

conversion into ketone **5**. Despite this, concerning the results of the study of the reaction mixture by NMR and GLC and the literature data one can suppose that hydrogenation of furfural proceeds *via* the routes presented in Scheme 1.

The quantitative chromatographic analysis of the reaction mixture shows that compounds **3**, **6**, and **7** are the main products in aqueous-phase hydrogenation of furfural over PdRu/CNTs at 473 K and a pressure of 8 MPa. A complete conversion of furfural is already observed 1 h after the onset of the reaction with alcohol **7** predominating among the products (Fig. 2). The subsequent hydrogenation of ketone **5** increases the selectivity towards alcohol **7** up to 77%. In the presence of monometallic Pd/CNTs and Ru/CNTs catalysts, albeit complete con-

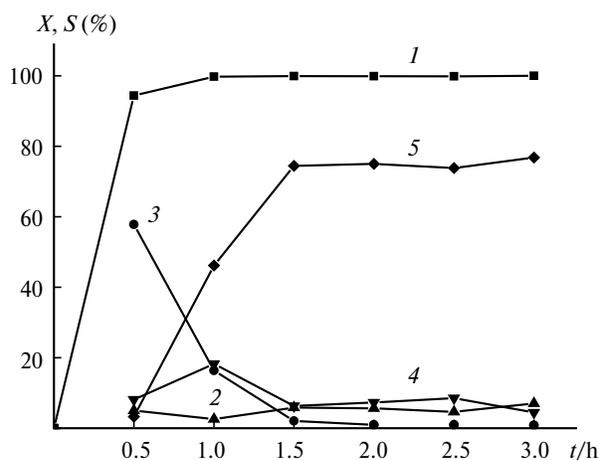


Fig. 2. Conversion (*X*) of furfural (**1**) and selectivity (*S*) of compounds **3** (**2**), **5** (**3**), **6** (**4**), and **7** (**5**) during aqueous-phase hydrogenation of furfural over PdRu/CNTs catalyst at a temperature of 473 K and a pressure of 8 MPa.

version of furfural occurs (473 K, 8 MPa), the yield of alcohol **7** does not exceed 18% 3 h after the onset of the reaction. In the case of ruthenium-containing catalyst, ketone **5** is a predominant product; its yield reached 51%. As noted above, aqueous-phase hydrogenation over the noble metal based catalysts allows to selectively produce ketone **5** but the subsequent reduction with alcohol **7** formation is usually suppressed.^{11,12,16} A comprehensive search among the published literature shows that the 5%Ru/C catalyst, which stands out for the highest activity among the other noble metal supported systems, is unsuitable to synthesize alcohol **7** selectively (the maximum yield was 47%).^{3,26}

To explain the enhanced activity of the bimetallic PdRu/CNTs catalyst in aqueous-phase hydrogenation of furfural to alcohol **7**, we employed the results of high resolution transmission electron microscopy (HR TEM) and XPS study of this sample which were obtained recently.¹⁸ It was established that the joint reduction of Pd and Ru precursors supported on CNTs is accompanied by interaction with each other and formation of PdRu alloy. In comparison with the monometallic Pd/CNTs and Ru/CNTs samples, PdRu/CNTs catalyst is characterized with smaller supported bimetallic particles (average size of 1.6 nm) and, accordingly, a larger fraction of the active sites available for the reactant molecules. In addition, formation of alloy prevents an enlargement of the bimetallic particles under the conditions of catalytic reaction and ensures a stable performance of the catalyst.^{19,27,28} XPS data provide evidence that introduction of ruthenium into the catalyst increases a fraction of electron deficient forms of palladium which can act as electrophilic sites for adsorption and activation of carbonyl compounds.²⁹ In terms of the electronic factor, the enhanced activity of bimetallic PdRu/CNTs catalyst in the aqueous-phase hydrogenation of furfural can be a result of facilitation of polarization of the C=O bond in the substrate first and then in ketone **5**.

The yield of the products of hydrogenation of alcohol **1** (mainly compounds **3** and **6**) is low when both bimetallic PdRu/CNTs and monometallic Pd/CNTs and Ru/CNTs catalysts were used under the same conditions. In all cases the reaction route involving water is predominant. Apparently, the reason might be the conditions applied in this work (473 K, 8 MPa) which are favorable for water implication into Piancatelli rearrangement. Under considerably milder conditions (<363 K, <2 MPa), water does not participate in the reaction and compounds **1** and **3** are the main products of aqueous-phase hydrogenation of furfural.^{30,31}

Therefore, bimetallic 1.5%PdRu/CNTs catalyst was proved to be highly active in aqueous-phase hydrogenation of furfural to alcohol **7**. Under the chosen conditions (473 K, 8 MPa) the selectivity towards the product of interest reaches 77% at a complete conversion of furfural.

High performance of the studied catalyst may be attributed to changes in electronic state and dispersion of the supported metals caused by their interaction and formation of Pd–Ru alloy. Further study will be focused on optimization of the catalyst composition (nature of carbon support, content and ratio of the supported metals) and conditions of the catalytic reaction enabling production of alcohol **7** with enhanced selectivity.

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