# Nanoheterogeneous Ruthenium-Containing Catalysts Based on Dendrimers in the Hydrogenation of Aromatic Compounds under Two-Phase Conditions

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Abstract—Nanoheterogeneous catalysts based on ruthenium nanoparticles dispersed in crosslinked dendrimer matrixes with a size of polymer particles of 100-500 nm show high activity in the hydrogenation of aromatic compounds under two-phase conditions. The addition of water to the reaction medium exerts a strong promoting effect on the activity of the catalysts: The turnover frequency increases by a factor of 3-90depending on the substrate. When bimetallic (PdRu) nanoparticles are incorporated into the catalyst composition, the rate of benzene hydrogenation increases while the rate of transformation of substituted benzenes decreases.

*Keywords:* catalytic hydrogenation, aromatic compounds, two-phase catalysis, bimetallic nanoparticles, dendrimers, ruthenium, palladium

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The hydrogenation of aromatic compounds is one of the most important processes in the modern petrochemical industry: Such compounds as cyclohexane, cyclohexene, and naphthene hydrocarbons are obtained via this process [1-2]. The process has acquired a considerable role because of the toughening of ecological requirements for gasoline and diesel fuels [3-5].

Two-phase catalysis, which combines such advantages as the ability to perform reactions under mild conditions, the use of water as a "green solvent," and the feasibility of catalyst reuse, is of special interest [6]. The main disadvantage of this approach is that the rate of reaction is moderately high because of the poor solubility of aromatic compounds in water.

It is possible to employ amphiphilic nanosized metal particles dispersed in water, particularly ruthenium nanoparticles, stabilized by cyclodextrins [7–9], calixarenes [10], and quaternary ammonium salts [5]. In this case, the catalytic activity increases due to the immediate approach of metal sites and substrate molecules (including the formation of "guest—host" complexes [8]) and a large surface area of the dispersed catalytic system. However, as a rule, the turnover frequency (TOF) does not exceed several hundreds of inverse hours [5, 7–8]. The use of conventional heterogeneous catalysts based on ruthenium nanoparticles stabilized by tetramethylguanidine immobilized in the pores of montmorillonite makes it possible to attain TOF values on the order of 4000  $h^{-1}$  with the 100% conversion of benzene [11].

A higher efficiency is exhibited by systems in which nanoparticles are dispersed with the use of amphiphilic polymers, such as polyvinylpyrrolidone (PVP) [11–15], polyethyleneimine [6], and dendrimers [16]. As an example, in the presence of Ru/PVP catalysts the values of specific catalytic activity (in terms of absorbed hydrogen) were as high as 45000 h<sup>-1</sup> for benzene, 30000 h<sup>-1</sup> for ethylbenzene, 16000 h<sup>-1</sup> for anisole [12], and 21000 h<sup>-1</sup> for phenol [13].

Catalysts based on metal nanoparticles dispersed in the particles of crosslinked dendrimer matrixes with a size of polymer particles of 100-500 nm were described in [16-18]. Ruthenium-containing catalysts exhibited an extremely high activity with respect to phenols in water: In their presence the turnover frequency was as high as  $2775 h^{-1}$  for phenol and  $80727 \text{ h}^{-1}$  for resorcinol [16]. In this case, the polymer matrix served as a dispersion medium for metal nanoparticles. Simultaneously the matrix was highly permeable for substrates in the presence of water and provided a high activity of the system in the hydrogenation of water-soluble molecules, especially diatomic phenols. At the same time, in the absence of water these catalysts demonstrated a rather low activity in the hydrogenation of aromatic hydrocarbons [18].

This study presents data that suggest that the activity of such nanosized catalysts in the hydrogenation of aromatic hydrocarbons may be increased considerably in the presence of water in a two-phase system.

In addition, the effect of an additional metal (palladium) incorporated into the active phase on the efficiency of such catalysts was investigated. The use of two metals in an alloy frequently facilitates a gain in the activity of the catalyst and an increase in selectivity for certain products [19]. One of the earliest publications concerning the use of bimetallic alloys in catalysis applies to the monomerization of dicyclopentadiene and subsequent hydrogenation of the formed cyclopentadiene in the presence of the PdRu membrane catalyst [20]. It was shown that a bimetallic membrane catalyst that contains 9.8% Ru in the alloy is the most efficient in the monomerization and subsequent hydrogenation of dicyclopentadiene and that cyclopentene with a yield of up to 90% prevails in the reaction products.

Heterogeneous PdRh catalysts were active in the hydrogenation of both benzene [21] and polysubstituted (diphenyl- and triphenylbenzenes) and condensed aromatic compounds (naphthalene, anthracene, terphenylene, etc.) [22]. In both cases, efficiency was achieved through the interaction of palladium nanoparticles that were preliminarily encapsulated inside pores with semimobile rhodium complexes immobilized in the same place and the spillover of adsorbed hydrogen atoms that occur between them [21]. The reduction of complexes and the formation of nanoparticles occurred in this case either directly during hydrogenation of aromatic substrates or in the course of preliminary activation of the catalyst.

Heterogeneous PdRu catalysts supported on mesoporous SiO<sub>2</sub> of the SBA-15 type manifested high activity in the hydrogenation of benzene, cyclooctadiene, norbornene, and cyclododecatriene [23]; when supported on mesoporous  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, they were active in the hydrogenation of dimethyl terephthalate [24]. In both cases, the highest efficiency was exhibited by the catalysts that contain palladium and ruthenium at equal molar ratios. Note that  $PdRu/\theta$ -Al<sub>2</sub>O<sub>3</sub> was found to be the most selective with respect to the main product, viz., cyclohexanedicarboxylic acid dimethyl ester [24]. On the other hand, in the hydrogenation of electrondeficient aromatic substrates (benzoic acid and terephthalic acid dimethyl ester), activity was exhibited by RuPt catalysts supported on mesoporous SiO<sub>2</sub> [23].

In this study, the behaviors of nanosized Ru and PdRu particles dispersed in a network of crosslinked PPI dendrimers were compared in the two-phase hydrogenation of various aromatic hydrocarbons.

## EXPERIMENTAL

#### Compounds Used in This Study

The reagents used as initial and reference compounds were as follows: benzene (Irea 2000, analytical grade), toluene (Khimmed, special-purity grade), ethylbenzene (Reakhim, high-purity grade), *p*-xylene (Reakhim, high-purity grade), *o*-xylene (Khimmed, analytical grade), *n*-butylbenzene (Reakhim, highpurity grade), *sec*-butylbenzene (Reakhim, highpurity grade), *tert*-butylbenzene (Reakhim, highpurity grade), 1-ethyl-4-isopropylbenzene (Reakhim, high-purity grade), naphthalene (Reakhim, highpurity grade), 1-methylnaphthalene (Aldrich, 95%), and tetralin (Aldrich, 97+%).

The G1–HMDI–Ru catalyst (a catalyst based on the first-generation dendrimer DAB(NH<sub>2</sub>)<sub>4</sub> (G1) crosslinked by hexamethylene diisocyanate (HMDI) and G3–HMDI–Ru catalyst (a catalyst based on the third-generation dendrimer DAB(NH<sub>2</sub>)<sub>16</sub> (G3) crosslinked by hexamethylene diisocyanate) were synthesized as described in [16] and [18].

The bimetallic PdRu catalyst was synthesized using the following compounds: ruthenium(III) chloride (Aldrich, 45–55% Ru content), palladium(II) acetate (Aldrich, 99.9+%), and sodium borohydride (Aldrich,  $\geq$ 98%). Support G3–HMDI (third-generation dendrimer DAB(NH<sub>2</sub>)<sub>16</sub> crosslinked by hexamethylene diisocyanate) was synthesized as described in [16] and [18].

#### Instruments and Methods

Transmission electron microscopy (TEM) studies were performed on a LEO912 AB OMEGA electron microscope at a voltage of the electron tube of 100 kV. High-resolution TEM analysis was conducted on a JEM-2100F (Jeol Ltd., Japan) instrument at a voltage on the electron tube of 200 kV. The average size of the particles was calculated via treatment of the obtained micrographs with the Image J program.

X-ray photoelectron spectroscopy (XPS) studies were performed on an LAS-3000 instrument equipped with a photoelectron analyzer with the OPX-150 retarding potential. Photoelectrons were excited by X-ray radiation of the aluminum anode (Al<sub>K $\alpha$ </sub> = 1486.6 eV) with a voltage on the tube of 12 kV and an emission current of 20 mA. Photoelectron peaks were calibrated relative to the 1s line of carbon with a bond energy of 285 eV.

The amount of palladium was determined by the method of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Interpid II XPL instrument (Thermo Electron Corp., United States) under radial and axial observations at wavelengths of 310 and 95.5 nm.

The amount of ruthenium in the samples was measured by UV-visible spectroscopy on an Agilent UV-Vis 8453 instrument [25]. For this purpose, a series of aqueous calibration solutions of RuCl<sub>3</sub> (10-mL each volume) with concentrations of 0.02, 0.03, 0.05, and 0.08 mg/mL were prepared. Ruthenium-containing 2.5-mg samples (G3–HMDI–Ru), 1-mg samples

(G1-HMDI-Ru), and 1.5-mg samples (G3-HMDI-PdRu) were treated with the mixture of 2 mL of concentrated HCl (SigmaTech, reagent grade) and 2 mL of 30%  $H_2O_2$  (Aldrich). The volumes of the resulting solutions were adjusted to 10 mL With distilled water. Then, 10 mL of 0.015 l aqueous solution of 1,10-phenanthroline (Lachema, 98%) was added to each calibration solution and sample solution. The solutions acquired a maize-yellow color. To prepare complexes of Ru<sup>2+</sup>, 0.4-0.6 g of hydroxylamine hydrochloride (Reakhim, high-purity grade) was added to each solution. When the solutions were heated on a water bath at 100°C for 2 h, their color changed to orange-yellow. The amount of ruthenium was determined from the intensity of the absorption band at 444–450 nm ( $\epsilon = 1.5 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ ), which corresponded to the  $[Ru(phen)_3]^{2+}$  complex [26]).

The products of catalytic experiments were analyzed by gas-liquid chromatography with a ChromPack CP9001 gas chromatograph equipped with a flame-ionization detector and a 30 m  $\times$  0.2 mm capillary column packed with a SE-30 grafted phase. Chromatograms were analyzed with the Maestro 1.4 program. Conversion was determined from a change in the relative areas under the peaks of the substrate and reaction products.

#### Synthesis of the Bimetallic Palladium–Ruthenium Catalyst

A one-neck round-bottom 100-mL flask equipped with a magnetic stirrer and a reflux condenser was loaded with the G3–HMDI (300 mg) support and distilled water (75 mL). After the addition of ruthenium(III) chloride (92 mg, 0.45 mmol) and palladium(II) acetate (100 mg, 0.45 mmol) to the resulting suspension, its color rapidly changed to black. The reaction was conducted for 12 h at room temperature and the reaction mixture was evaporated to dryness on a rotor evaporator. The as-obtained black powder precipitate (400 mg, a yield of the first stage of 81%) was placed in a 50-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser and suspended in a mixture of ethanol (35 mL) and water (10 mL). Sodium borohydride (182 mg, 4.8 mmol) was then added in portions to the resulting suspension. The reaction mixture acquired a saturated black color and the intense evolution of gas bubbles was observed. The reaction was conducted for 12 h at room temperature, and the precipitate was separated from the solution that contained the residues of the intact sodium borohydride and the formed borax via centrifugation, washed three times with water and ethanol, and dried in air. The yield of the resulting material was 325 mg (82.5%).

XPS data (eV) was as follows: 279.4 ( $\text{Ru}^0 3\text{d}_{5/2}$ ), 280.3 ( $\text{Ru}/\text{RuO}_x 3\text{d}_{5/2}$ ), 281.1 ( $\text{RuO}_2 \text{ or } \text{RuCl}_3 3\text{d}_{5/2}$ ), 281.7 ( $\text{RuCl}_3 \times x\text{H}_2\text{O} \text{ or } [\text{Ru}^{2+}]_{\text{bound}} 3\text{d}_{5/2}$ ), 282.2

 $([Ru^{3+}]_{bound} 3d_{5/2}); 282.3 (C 1s, 1.6\%, C \equiv Ru/Pd),$ 283.4 (C 1s, 2.2%, C=N), 284.7 (C 1s, 6.1%, C-C, C–H), 286.2 (C 1s, 2.3%, C–N), 287.4 (C 1s, 1.5%, –NH–C(=O)–NH–), 288.5 (C 1s, 0.9%, –NH– C(=O)-NH-C(=O)-NH-), 289.6 (C 1s, 0.3%, -NH-C(=O)-NH-C(=O)-NH- or -NH-C(=O)-OH; 284.3 (Ru<sup>0</sup> 3d<sub>3/2</sub>), 285.0 (Ru/RuO<sub>x</sub>)  $3d_{3/2}$ ), 285.9 (RuO<sub>2</sub> or RuCl<sub>3</sub>  $3d_{3/2}$ ), 286.7 (RuCl<sub>3</sub> ×  $xH_2O \text{ or } [Ru^{2+}]_{bound} 3d_{3/2}), 287.6 ([Ru^{3+}]_{bound} 3d_{3/2});$ 335.1 (Pd<sup>0</sup> 3d<sub>5/2</sub>, 0.15%), 336.8 (PdO<sub>x</sub> 3d<sub>5/2</sub>, 0.32%), 338.4 ( $Pd^{2+}$  3d<sub>5/2</sub>, 0.50%), 339.7 ( $[Pd^{2+}]_{bound}$  3d<sub>5/2</sub>, (0.33%), 340.4 (Pd<sup>0</sup> 3d<sub>3/2</sub>, 0.16%), 340.9 (Pd<sup>2+</sup> 3d<sub>5/2</sub>) sat, 0.21%), 341.8 (PdO<sub>x</sub>  $3d_{3/2}$ , 0.40%), 343.4 (Pd<sup>2+</sup> 3d<sub>3/2</sub>, 0.55), 345.15 ([Pd<sup>2+</sup>]<sub>bound.</sub> 3d<sub>5/2</sub>, 0.44%), 346.8  $(Pd^{2+} 3d_{3/2}, sat, 0.23\%), 348.0 ([Pd^{2+}]_{bound} 3d3_{5/2}, sat,$ 0.10%); 396.6 (N 1s, 3.7%, N≡Pd/Ru), 398.3 (N 1s, 6.3%, -C=N-),399.6 (N 1s. 1.2%.  $-NCH_2CH_2CH_2N-,$  $-CH_2-NH-C(=O)-NH-$ CH<sub>2</sub>-), 401.0 (N 1s, 6.5%, NH<sub>3</sub>R<sup>+</sup>, -C=NH<sup>+</sup>-, -NH-C(=O)-NH-C(=O)-NH-,NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N $\rightarrow$ Pd/Ru<sup>n+</sup>), 403.3 (N 1s, 2.7%,  $NR_{4}^{+}, R_{3}N^{+}\rightarrow O^{-}), 405.3 \text{ (N 1s, } 0.6\%, -NCH_{2}CH_{2}CH_{2}N^{-}, -NH^{-}C(=O)^{-}NH^{-}, \text{ sat)};$ 459.6 (Ru<sup>0</sup> 3p<sub>3/2</sub>, 0.35%), 461.6 (Ru/RuO<sub>x</sub> 3p<sub>3/2</sub>, 0.65%), 463.3 (RuO<sub>2</sub> or RuCl<sub>3</sub> 3p<sub>3/2</sub>, 1.21%), 464.8  $(\text{RuCl}_3 \times x\text{H}_2\text{O or } [\text{Ru}^{2+}]_{\text{bound}} 3p_{3/2}, 0.60\%), 466.1$ ([Ru<sup>3+</sup>]<sub>bound</sub> 3p<sub>3/2</sub>, 0.18%); 528.3 (O 1s, 3.5%, O-Pd<sup>0</sup>), 529.8 (O 1s, 10.9%, O-Pd<sup>II</sup>), 531.5 (O 1s, 32.4%,  $-CH_2-NH-C(=0)-NH-CH_2-)$ , 533.20 (O 1s, 7.8%, H<sub>2</sub>O), 534.5 (O 1s, 2.3%, H<sub>2</sub>O...-NH-C(=O)-NH-), 540.2 (O 1s, sat, 0.8%); 532.2 (Pd<sup>0</sup>  $3p_{3/2}$ ), 533.1 (PdO<sub>x</sub>  $3p_{3/2}$ ), 534.0 (Pd<sup>2+</sup>  $3p_{3/2}$ ), 534.9  $([Pd^{2+}]_{bound} 3p_{3/2}), 535.8 (Pd^{2+} 3p_{3/2}, sat).$ 

The contents of metals were found to be Ru, 8% and Pd, 10%.

# Technique of Catalytic Experiments

The catalyst and substrate were placed at the desired ratio in a steel thermostatically controlled autoclave equipped with a stirrer. In experiments performed in the presence of water, the latter was added at a ratio of 1 mL of water per mL of substrate. The autoclave was sealed, filled with hydrogen to a pressure of 10 or 30 atm, and connected to a thermostat. The reaction was conducted at 85 or 90°C. The autoclave was then cooled below room temperature and unsealed. The reaction products were analyzed by gasliquid chromatography.

The activity of catalysts (TOF) was estimated as the amount of converted substrate per Ru mol per time unit:

$$\Gamma OF = \frac{v_{substr} \times \omega}{v_{Ru} \times t},$$

where  $\omega$  is the conversion of substrate expressed in unity fractions.

Catalyst			Surface atomic concentrations, %						
	Metal content, %	Average size of particles, nm	С	N	0	Ru	Ru 3p <sub>3/2</sub> , % (eV)		
							Ru <sup>0</sup>	RuO <sub>2</sub> , RuCl <sub>3</sub>	[Ru <sup>3+</sup> ] <sub>bound</sub>
G1–HMDI–Ru	34.6	3.8 ± 1.1	26.1	11.9	41.6	20.4	29.9 461.5)	48.8 (463.5)	21.3 (465.9)
G3–HMDI–Ru	9.4	$0.9\pm0.2$	18.9	26.8	45.6	8.7	15.0 (461.0)	58.5 (463.4)	26.4 (466.1)

**Table 1.** The physicochemical characteristics of the synthesized catalysts [16]

Table 2. The physicochemical characteristics of the G3-HMDI-PdRu catalyst

Content	Content	itent d nm	Surface atomic concentrations, %					
of Pd, %	of Ru, %	<i>u</i> , IIII	С	Ν	0	Pd		Ru
10	8	$0.8 \pm 0.1$	14.9	21.0	57.7	3.4		3.0
	Ru 3p <sub>3/2</sub> , at % (eV)							
Ru <sup>0</sup>		Ru/RuO <sub>x</sub>	RuO <sub>2</sub> o	r RuCl <sub>3</sub>	$\operatorname{RuCl}_3 \times x \operatorname{H}_2 \operatorname{Cl}_3$ or $[\operatorname{Ru}^{2+}]_{\text{bound}}$	<b>)</b> 1	[Ru <sup>3</sup>	<sup>3+</sup> ] <sub>bound</sub>
11.9 (459	9.6)	21.9 (461.6)	40.3 (	463.3)	20.7 (464.8)		6.1 (466.1)	
Pd 3d <sub>5/2</sub> , at % (eV)								
$Pd^0$		$PdO_x$	$Pd^{2+}$		[Pd <sup>2+</sup> ] <sub>bound</sub>		Pd <sup>2</sup>	<sup>2+</sup> , sat
9.9 (335	.1)	21.1 (336.8)	33.0 (338.4)		21.7 (339.7)		14.2 (340.9)	

#### **RESULTS AND DICUSSION**

## Synthesis of Hybrid Catalysts Based on Ruthenium Nanoparticles and Alloys Encapsulated in Crosslinked Dendrimer Networks

The synthesized materials, which consisted of ruthenium nanoparticles dispersed within crosslinked matrixes based on first- and third-generation dendrimers [16, 18], were characterized by the high density and uniform distribution of particles on the support surface. The average sizes of metal particles were 3.8 and 0.9 nm for the catalysts based on first- and third-generation dendrimers, respectively. The detailed characteristics of the samples are summarized in Table 1 [16]. The size of the matrix itself, in accordance with the TEM data, was from 100 nm to 2  $\mu$ m.

A similar synthesis technique was employed for the synthesis of the G3–HMDI–PdRu bimetallic catalyst. As a support, a network based on the third-generation dendrimers crosslinked by hexamethylene diisocyanate (NCO :  $NH_2 = 1 : 1$ ) was used. The alloy was created via the cocomplexation method according to the technique that was previously used for the synthesis of monometallic ruthenium catalysts [18] based on dendrimers at a nominal Pd-to-Ru ratio of 1 : 1. The physicochemical characteristics of the sample are listed in Table 2.

In accordance with the TEM data, G3–HMDI– PdRu is a highly dispersed material with a narrow particle size distribution (Fig. 1). The average diameter is 0.8–1.0 nm. This value is close to that obtained for the previously synthesized monometallic catalyst G3– HMDI–Ru [16]. Note that G3–HMDI–PdRu also features high density and uniform distribution of particles on the support surface because of the strong complexing ability of the support.

As shown by XPS (Fig. 2), both metals occur on the catalyst surface at an approximately equal proportion (3.4% for Pd and 3.0% for Ru), which correlates with their content in the catalyst volume (10% for Pd and 8% for Ru). For both metals, oxidized and complex forms prevail in the sample. The ratio of reduced and oxidized forms was approximately 1:2 for ruthenium  $([Ru^{0} + Ru/RuO_{x}]/[RuO_{2} + Ru^{3+}])$  and 1 : 9 for palladium  $(Pd^{0}/[PdO_{x} + Pd^{2+}])$ . The higher content of oxidized forms for palladium, despite a high affinity of ruthenium to oxygen [27, 28], may be explained by the incomplete dissolution of palladium in the form of palladium acetate in the water that was used as a reaction medium during synthesis of the catalyst. As a consequence, the ions of palladium (in the form of corresponding complexes) predominantly concentrated in the volume of the amphiphilic support; as a result,



Fig. 1. The G3–HMDI–PdRu catalyst: (a) TEM micrograph and (b) size distribution of particles.

their further reduction by sodium borohydride was hindered.

The above suggestion is confirmed by the XPS spectrum of the 1s line of nitrogen (Fig. 2b), in which the predominant signals are as follows: a signal that corresponds to the imine complexes of zero-valent metals (398.3 eV,  $-CH_2-CH=NH\rightarrow Pd/Ru^0$ ), which formed as a result of reduction of the latter by the amino groups of dendrimers [29], and a signal that corresponds to the amine complexes of bound metal ions (401.0 eV,  $-CH_2-CH-NH_2 \rightarrow Pd/Ru^{n+}$ ) [30]. It should be emphasized that the observed picture is not typical for the catalysts based on dendrimer networks that contain metals in the reduced or partially reduced state, where the main fraction of nitrogen that occurs on the surface is due to the inner amino groups of dendrimers and urethane fragments [16]. In this case, the shift in bond energies on passage from the support to the catalyst is as a rule practically invisible because of the similarity of their values for the -CH<sub>2</sub>-CH- $NH_2 \rightarrow Pd/Ru^0$  [31, 32] and  $-CH_2 - NH - C(=O) - OH_2 - OH_2$ NH-CH<sub>2</sub>-[33-35] fragments.

A higher ( $[Ru^0 + Ru/RuO_x]/[RuO_2 + Ru^{3+}]$ ) ratio is also noteworthy for the bimetallic catalyst (1 : 2) relative to that of the monometallic catalyst (1 : 5.7) on the analogous support. Against the background of a well-defined dominance of the oxidized forms for palladium in G3–HMDI–PdRu, it may be assumed that the latter, along with sodium borohydride, is involved in the reduction of ruthenium and probably decelerates the oxidation process during storage in air, as is typical for ruthenium nanocatalysts [36].

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# Hydrogenation of Aromatic Compounds in the Presence of Dendrimer-Based Ru Catalysts

Materials based on ruthenium nanoparticles and PPI dendrimers crosslinked by hexamethylene diisocyanate that were used in the hydrogenation of phenols [16] were tested in the hydrogenation of aromatic compounds. Hydrogenation was conducted at pressures of 5, 10, and 30 atm and temperatures of 85– 90°C both in the presence of water and in its absence.

As in the case of phenols, the activity of both catalysts depended on such factors as substrate size and geometry, dendrimer generation, and the electronic effects of substituents. The main products were cyclohexane and its derivatives with a selectivity of 97-100%. The experimental data are summarized in Tables 3-6. Some of these results were reported in [18].

As is seen from Tables 3 and 4, the ruthenium catalysts based on dendrimers efficiently hydrogenate aromatic compounds under two-phase conditions, including reduced pressures (Table 3). As an example, the turnover frequency for the catalyst G1–HMDI–Ru in the hydrogenation of benzene attains even  $5000 \text{ h}^{-1}$ ; quantitative conversions become attainable at high substrate/Ru ratios and pressures and smaller reaction times (Table 3).

As in the case of phenols [18], the substrate size and the negative dendrite effect [37] still retained their impacts on the activity of the catalyst; however, the latter value does not decline as abruptly upon replacement of benzene by its alkyl-substituted derivatives, such as toluene and ethylbenzene (Fig. 3). Note that now the electronic effects of substituents insignifi-



**Fig. 2.** The XPS spectra of G3–HMDI–PdRu: (a) 3p line of ruthenium, (b) 3d line of palladium, and (c) 1s line of nitrogen.

cantly affect the activity of the catalyst but meet the steric demand solely.

The effect of water on the rate of hydrogenation of aryl-containing substrates was previously explained by



**Fig. 3.** The hydrogenation of aromatic compounds in the presence of Ru catalysts based on dendrimers in an aqueous medium. Reaction conditions:  $85^{\circ}$ C and  $p(H_2) = 30$  atm.

the Ru-catalyzed hydrolysis of the crosslinked dendrimer matrix, which leads to a reduction in steric hindrances around catalytic sites and, as a consequence, facilitates the substrate access to them [16]. In other words, we obtain water-dispersed fragments of the polymer matrix that function as peculiar microreactors that contain inside ruthenium nanoparticles and are able to capture substrate hydrophobic molecules [14]. Nevertheless, if in the case of linear polyvinylpyrrolidone, an increase in chain length and, as a result, in the molecular mass of the polymer leads to a gain in the stability and activity of the catalytic system [12], then in the case of branched polypropyleneimine dendrimers, in contrast, the activity decreases as before because steric hindrances and negative dendrite effect increase with the increasing molecular mass and generation of the dendrimer.

Another factor that contributes to an increase in the catalytic activity in the presence of water is the "washing-off" of adsorbed water and other oxide layers from the surface of ruthenium nanoparticles, which prevents the competitive adsorption of nonpolar substrates [38]. Hence, the presence of water in the reaction medium assists in adsorption and, at the same time, accelerates the hydrogenation of aromatic compounds.

In addition, note that the increase in the activity in the presence of water is more pronounced for the nonpolar aromatic compound than that for more polar phenols [18]. This finding may be explained by the fact that the dendrimer network acts as an amphiphilic dispersion medium that simultaneously interacts with water and the aromatic substrate [14]. The combination of these factors facilitates both the desorption of water during activation of the surface of nanoparticles and the subsequent adsorption of nonpolar aromatic substrates. As a consequence, the rate of their hydrogenation increases considerably.

Substrate	Substrate/Ru, mol/mol	<i>t</i> , h	Conversion, %	TOF, $h^{-1}$
	160	6	100	27
		2	100	80
	800	2	100	400
Benzene		0.5	100	1600
		0.5	95*	1510
	2400	0.5	97.5	4675
	4795	0.5	52	4975
	135	6	100	22
		2	100	67
Toluene	670	2	100	400
		0.5	100	1610
	2010	0.5	47.5	2295
	116	6	100	19.5
		2	100	58
Ethylbenzene	580	2	100	396.5
		0.5	100	1320
	1750	0.5	29	1380
	117	6	100	19.5
. V.I		2	100	58.5
o-Aylene	585	2	98	390
		0.5	13	207
<i>p</i> -Xylene	116	6	100	19.5
		2	100	58
	580	2	100	396
		0.5	22	350
Dutulhangana	200	6	25	8.5
Butylbenzene		2	15.5	15.5

Table 3. Hydrogenation of aromatic compounds in the presence of the G1-HMDI-Ru catalyst under two-phase conditions

Reaction conditions:  $85^{\circ}$ C, 30 atm of H<sub>2</sub>, and substrate/water = 1 : 1 (vol/vol). \* 10 atm of H<sub>2</sub>.

The use of the catalyst based on the third-generation dendrimer, G3–HMDI–Ru, caused a marked reduction in the rate of hydrogenation (Table 4) relative to that of G1–HMDI–Ru (Table 3). The activities of both catalysts are compared in Fig. 3. As an example, in the case of G3–HMDI–Ru quantitative conversions are attainable only for benzene (Table 3) even for a rather long time (6 h) and the observed TOF values are much lower than those previously obtained in the presence of the same catalyst for phenols [16]. Such a sharp change in the behavior of the catalyst may be associated with not only a very strong negative dendrite effect [37], as observed on passage from the support based on the first-generation dendrimer to that based on the third-generation dendrimer (Fig. 3), but also with a change in the hydrophobicity of the support itself. As an example, in the case of G1– HMDI–Ru, the end amino groups of the dendrimer next to the center are now involved in bonding with hydrophobic diisocyanates and, as a result, form a

Substrate	Substrate/Ru, mol/mol	<i>t</i> , h	Conver- sion, %	TOF, $h^{-1}$
Benzene	170	6	100	28
		2	94	80
		0.5	56.5	190
	845	2	55	230
Toluene	170	6	47	13
		2	44	38
		0.5	22	75
	850	2	19.5	83
Ethylbenzene	168	6	61	17
		2	57	48
		0.5	25	84
	840	2	24	100
o-Xylene	168	6	13	3.5
		2	11	9
<i>p</i> -Xylene	167.5	6	28.5	8
		2	25	21
Butylbenzene	162	6	49.5	13.5
		2	45.5	37
		0.5	24	78
	810	2	10	39.5

**Table 4.** Hydrogenation of aromatic compounds in the presence of the G3–HMDI–Ru catalyst under two-phase conditions

Reaction conditions:  $85^{\circ}$ C, 30 of atm H<sub>2</sub>, and substrate/water = 1 : 1 (vol/vol).

polyurethane network with an almost uniform distribution of hydrophobic and hydrophilic fragments.

In contrast, G3–HMDI–Ru is characterized by the presence of more defined hydrophobic and hydrophilic regions because the third-generation dendrimers that comprise the support contain a large amount of inner nitrogen atoms that are uninvolved in the formation of urethane groups with hexamethylene diisocyanate molecules and, therefore, are able to form hydrogen bonds. During hydrolysis of this network under the action of ruthenium nanoparticles end amino groups of dendrimers are released from urethane bonds; urethane groups from the side of binding agents are converted into carbamate ones. As a consequence, despite partial hydrolysis of the dendrimer matrix and reduction in steric hindrances surrounding catalytic sites, the hydrophobic aromatic substrate cannot be efficiently involved in the microreactors formed by hydrophilic residues of the above-mentioned dendrimer matrix; therefore, the rate of reaction declines.

As in the case of phenols [16], when the reaction is performed in the absence of water, the activities of both catalysts decrease appreciably (Table 5), although the reaction is conducted at a higher temperature (90°C). As an example, the turnover frequency for G1–HMDI–Ru now does not exceed 1500 h<sup>-1</sup> with respect to benzene (instead of 5000 h<sup>-1</sup> in presence of water). Increase in the size of substituents and in their amount caused a decrease in the conversion and turnover frequency, especially at high substrate/Ru ratios and smaller reaction times. Reduction in the pressure of hydrogen to 5 atm also led to a decrease in the catalytic activity. Nevertheless, conversions close to 100% could be obtained for a wide range of substrates.

Similar tendencies were observed when the reaction was performed in the absence of water with the use of the catalyst based on the third-generation dendrimer (Table 6). A decrease in the pressure of hydrogen resulted in a more distinct decline in the rate of reaction than that in the case of G1-HMDI-Ru [18]. In this case, increase in the reaction time and the catalyst concentration slightly affected the attained level of substrate conversion.

Hence, it may be assumed that in the presence of high-generation dendrimers used as stabilizing ligands both the adsorption of the aromatic substrate on the surface of ruthenium nanoparticles and the subsequent addition of hydrogen are rate-limiting stages.

Because *o*-xylene, for which tetralin is the structural analog, is hydrogenated to 100% in the presence of G1–HMDI–Ru in an aqueous medium, it was supposed that tetralin may be also hydrogenated under milder conditions. It was found that the activity of the dendrimer-based ruthenium catalysts in the absence of water grows significantly if the reaction is conducted at elevated temperatures (170°C) (Fig. 4).

Thus, for both catalysts the conversion of benzene achieved 60-70% within 2 h. Tetralin was hydrogenated by 95% over 6 h in the presence of the G1-HMDI-Ru catalyst and by 81% in the presence of G3-HMDI-Ru. In both cases, the dominant product in the hydrogenation of tetralin was *cis*-decalin, with a selectivity of 80-85%, as is typical for Ru catalysts [39].

The replacement of tetralin with a mixture of naphthalene and 1-methylnaphthalene (Fig. 4) caused a marked drop in conversions (down to 5-12% over 6 h). This effect may be associated with the size and rigid structure of condensed aromatic compounds. As a consequence, the latter meet substantial

Substrate	Hydrogenation in water, TOF, $h^{-1}$	Hydrogenation without water TOF, $h^{-1}$
Danzana	4975	1550
Denzene	1510*	17* [18]
Toluene	2295	67
Ethylbenzene	1380	65
o-Xylene	390	27
<i>p</i> -Xylene	395	53.5
Butylbenzene	15.5	6

Table 5. The effect of water on the activity of the G1–HMDI–Ru catalyst in the hydrogenation of aromatic compounds

Reaction conditions:  $85^{\circ}$ C, 30 atm of H<sub>2</sub>, and substrate/water = 1 : 1 (vol/vol), for hydrogenation with water; for hydrogenation at 90°C without water.

\* 5-10 atm of H<sub>2</sub>.

barriers from the crosslinked dendrimer matrix on their way to catalytic sites. Moreover, condensed aromatic rings are subjected to the action of a weak -M effect from each other; this creates additional hindrances to their adsorption on the surface of ruthenium nanoparticles. The lower turnover frequency for the G1-HMDI-Ru catalyst may be explained by an insufficiently high substrate/Ru ratio compared to G3-HMDI-Ru.

The addition of water to the reaction medium made it possible to attain quantitative conversions of tetralin even at a much lower temperature (90°C against 170°C). As an example, in the presence of the G1–HMDI–Ru catalyst a conversion of 90% was reached over 30 min and a conversion of 100% was achieved over 2 h at substrate/Ru ~170 (Fig. 5). In this case, the turnover frequency was 305 h<sup>-1</sup>. The main reaction product, as in the absence of water, was *cis*-decalin with a selectivity of up 85%. When the substrate/Ru ratio was changed to 850, the turnover frequency was increased 805 h<sup>-1</sup>; however, quantitative conversions were attainable only during a very long period of time (Fig. 5).

At the same time, naphthalene and 1-methylnaphthalene were hydrogenated in the presence of water at 90°C, as before, over 6 h with conversions of 2 and 4%, respectively. It appears that the conformational rigidity and the -M effect play the key role in the hydrogenation of these substrates and thus hamper their adsorption and diffusion even through a partially hydrolyzed dendrimer matrix. A lower conversion of naphthalene than that of 1-methylnaphthalene may probably be rationalized by the ability of naphthalene to sublime under the reaction conditions. The main products of naphthalene hydrogenation are tetralin with a selectivity of 65–70% and *cis*-decalin with a selectivity of 25–30%. For 1-methylnaphthalene, the main product is 5,6,7,8-tetrahydro-1-methylnaph-thalene with a selectivity of up to 80%.

G3–HMDI–Ru, which is more sensitive to the size, geometry, and conformational rigidity of the substrate, was tested only in the hydrogenation of tetralin. The conversion of this compound was as low as 13% (TOF ~4 h<sup>-1</sup>) in the presence of the above-mentioned catalyst (90°C, 40 atm of H<sub>2</sub>). This value is comparable with the conversion in the hydrogenation of *o*-xylene (Table 4).

**Table 6.** The effect of water on the activity of the G3– HMDI–Ru catalyst in the hydrogenation of aromatic compounds

Substrate	Hydrogenation in water, TOF, h <sup>-1</sup>	Hydrogenation without water TOF, h <sup>-1</sup>
Benzene	300	56
Toluene	83	3.5
Ethylbenzene	130	<1
o-Xylene	9	4.5
<i>p</i> -Xylene	21	3
Butylbenzene	78	0.5

Reaction conditions:  $85^{\circ}$ C, 30 atm of H<sub>2</sub>, and substrate/water = 1 : 1 (vol/vol), for hydrogenation with water; at 90°C without water.



**Fig. 4.** Hydrogenation of benzene and condensed aromatic compounds in the presence of Ru catalysts based on dendrimers. Reaction conditions:  $170^{\circ}$ C and  $p(H_2) = 30$  atm.

# Hydrogenation of Aromatic Compounds in the Presence of the Bimetallic Catalyst PdRu

The data on the hydrogenation of aromatic compounds in the presence of G3–HMDI–PdRu are presented in Table 7. As in the case of G3–HMDI–Ru, for G3–HMDI–PdRu conversions and activities decreased abruptly with the increasing substrate size. This observation may be explained by the use of sterically hindered third-generation dendrimers and the concomitant dendrite effect [37]. The presence of products of incomplete hydrogenation (cyclohexene and its derivatives) and isomerization (in the case of *o*- and *p*-xylenes) may be due to the presence of palladium in the active phase and, as a consequence, to a change in the electronic properties of the surface of



**Fig. 5.** Hydrogenation of tetralin in the presence of G1– HMDI–Ru under two-phase conditions. Reaction conditions: 90°C, 40 atm of H<sub>2</sub>, and V(substrate) = V(H<sub>2</sub>O).



**Fig. 6.** Comparison of the activities of G3–HMDI–PdRu and G3–HMDI–Ru in the hydrogenation of aromatic compounds. Reaction conditions:  $80^{\circ}$ C, 2 h, 30 atm of H<sub>2</sub>, and substrate/water = 1 : 1 (vol/vol).

nanoparticles [21, 39, 40]. A sharper (more than twofold) increase in activity relative to the monometallic catalyst (Fig. 6) may be apparently attributed to the synergistic effect of palladium and ruthenium in the melt [19, 21].

Palladium, which does not catalyze the hydrogenation of aromatic compounds under these conditions, serves as an additional source of adsorbed hydrogen that is further transferred on ruthenium atoms as a result of spillover. The drop in activity in the case of alkyl-substituted benzenes, in particular butylbenzene, may probably be explained as follows. For the hydrogenation reaction to be advantageous, the size of the area on the nanoparticle surface, which is composed of ruthenium atoms, should be sufficient to allow  $\pi$  adsorption of the aromatic compound and the simultaneous adsorption of hydrogen. As the size of the substrate and the number of its substituents increase, the size of the area should become accordingly larger. At the same time, the number of such adsorption sites on bimetallic particles turns out to be lower because of the surface "dilution" by palladium.

Materials based on ruthenium nanoparticles dispersed in crosslinked dendrimer matrixes manifested themselves as high-activity catalysts in the hydrogenation of aromatic compounds in two-phase systems water/substrate. Water, as an additional dispersion medium, exerted a strong promoting effect on the rate of hydrogenation due to a change in the properties of the dendrimer matrix, its partial hydrolysis, and facilitated reduction of the catalyst surface. The introduction of an additional metal into the catalyst with the analogous support (G3–HMDI–PdRu) leads to a marked gain in the rate of hydrogenation of benzene and a decrease in the rate of its transformation.

Substrate	Substrate/Ru, mol/mol	Conversion, %	TOF, $h^{-1}$	Products
	712	85	302	Cyclohexane 99% Cyclohexene 1%
		84*	299	Cyclohexane 99.5% Cyclohexene 0.5%
Benzene	1780	47.5	423	Cyclohexane 99% Cyclohexene 1%
		49*	436	Cyclohexane 98.5% Cyclohexene 1.5%
Toluene	715	20	71.5	Methylcyclohexane 99% Methylcyclohexene 1%
Ethylhonzono	723	18	(5.0	Ethylcyclohexane 99%
Ethylbenzene			63.0	Ethylcyclohexene 1%
	734	1**	3.7	Cis-1,2-Dimethylcyclohexane 6%
				Trans-1,2-Dimethylcyclohexane 65%
o-Xylene				<i>Cis</i> -1,4-Dimethylcyclohexane 4.5%
				Trans-1,4-Dimethylcyclohexane 10.5%
				Ethylcyclohexane 13.5%
	718	2	7.2	Cis-1,2-Dimethylcyclohexane 30%
				Trans-1,2-Dimethylcyclohexane 5%
<i>p</i> -Xylene				Cis-1,4-Dimethylcyclohexane 56%
				Trans-1,4-Dimethylcyclohexane 9%
Butylbenzene	730	2	7.3	Butylcyclohexane 100
Tatralia	840	E	21.0	Cis-Decalin 90%
Ietralin		3		Trans-decalin 10%

Table 7. Hydrogenation of aromatic compounds in water in the presence of the G3–HMDI–PdRu catalyst

Reaction conditions:  $80^{\circ}$ C, 2 h, 30 atm of H<sub>2</sub>, and substrate/water = 1 : 1 (vol/vol).

\* 10 atm of H<sub>2</sub>.

\*\* Isomerization of substrate, 8% (PhEt).

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