# A Nanospherical Mesoporous Ruthenium-Containing Polymer as a Guaiacol Hydrogenation Catalyst

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Abstract—A hybrid catalyst is synthesized using ruthenium nanoparticles deposited on a nanospherical mesoporous polymer. Catalytic properties are studied in guaiacol hydrogenation at a temperature of  $200-250^{\circ}$ C and a hydrogen pressure of 5.0 MPa. Effect of solvent and catalytic additives on the reaction is investigated. It is shown that the synthesized catalyst exhibits the highest activity in guaiacol hydrodeoxygenation in the two-phase system water/*n*-dodecane and when the reaction is carried out in the presence of scandium triflate.

*Keywords*: mesoporous polymer, nanospheres, nanoparticles, ruthenium, guaiacol, hybrid catalyst, hydrogenation

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Selection of a support for an active component is of prime importance for the design of efficient heterogeneous catalysts [1-3]. The activity of the catalytic system is affected by the distribution of nanoparticles on the support surface, their size, and the accessibility of active sites. Catalysts based on metal nanoparticles immobilized in the pores of ordered porous organic or organometallic structures can potentially exhibit high activity and selectivity owing to the possibility to control the support nature and structure [4-6].

Systems based on metal nanoparticles immobilized within phenol-formaldehyde polymers manifest high activity in the hydrogenation of acetylenes, dienes, and phenolic and polyaromatic compounds [7–10]. However, these materials are characterized by the presence of large particles (up to 2  $\mu$ m) and a wide particle size distribution. Compared with these materials mesoporous nanospherical materials prepared by hydrothermal synthesis at low concentrations of initial reagents are characterized by the presence of short mesochannels and a smaller size of particles (100–200 nm). Catalytic sites immobilized in them are more accessible to reactants, which increases the mass transfer rate and the catalyst activity [11–13].

Thus, the goals of this study were the synthesis of Ru-containing hydrogenation catalyst NSMP-Ru immobilized in pores of the ordered mesoporous phenol-formaldehyde polymer and the investigation of its catalytic properties in the hydrogenation of guaiacol bio-oil model compound.

#### EXPERIMENTAL

#### Initial Compounds

The reagents were phenol (Reakhim, high-purity grade), formaldehyde (37% aqueous solution, Sigma-Aldrich), triblock copolymer Pluronic F127 ( $M_n = 12600, EO_{106}-PO_{70}-EO_{106}$ , Aldrich), sodium hydroxide (IREA 2000, reagent grade), sodium borohydride (Acros Organics, 98%), ruthenium(III) chloride (OAO Aurat, 47.8%), guaiacol C<sub>7</sub>H<sub>8</sub>O<sub>8</sub> (Sigma-Aldrich, Kosher, 98%), orthophosphoric acid (85 wt %), sulfuric acid (IREA 2000, reagent grade), magnesium oxide (Sigma-Aldrich, 97%), and scandium(III) triflate (Sigma-Aldrich, 99%). Ethanol (IREA 2000, analytical grade) and *n*-dodecane (Sigma-Aldrich, 99%) were used as solvents.

#### Instruments and Analytical Procedures

Nitrogen adsorption/desorption isotherms were measured at a temperature of 77 K on a Gemini VII 2390 surface area analyzer. Before measurements the samples were outgassed at a temperature of 110°C for 5 h. The specific surface area ( $S_{\text{BET}}$ ) was calculated by the Brunauer–Emmett–Teller (BET) method using the adsorption data obtained in the relative pressure ( $P/P_0$ ) range of 0.04–0.2. The pour volume and pore size distribution were assessed from the adsorption branches of the isotherms in terms of the Barrett– Joyner–Halenda (BJH) model. Transmission electron microscopy (TEM) studies were carried out on a LEO912 AB OMEGA microscope. TEM images were processed and the average particle size was determined using the program ImageJ. X-ray photoelectron microscopy (XPS) measurements were conducted on a PHI5500VersaProbeII X-ray photoelectron spectrometer. Photoelectrons were excited using the  $AlK_{\alpha}$ X-ray emission of the aluminum anode (1486.6 eV). The binding energy scale was calibrated against the C1s line of aromatic carbon ( $E_{\rm b} = 284.7$  eV). The survey spectra were measured in the range of 0-1100 eV at an analyzer pass energy  $(E_{\text{pass}})$  of 117.4 eV with a step of 1 eV. High-resolution spectra were taken at  $E_{\text{pass}} =$ 23.5 eV with a step of 0.2 eV. Solid-state CP/MAS <sup>13</sup>C and <sup>1</sup>H NMR studies were carried out on a Varian NMR Systems instrument operating at a frequency of 125 MHz in the pulsed mode at a MAS frequency of 10 kHz. The quantitative determination of ruthenium in the catalyst samples was conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Interpid II XPL instrument (Thermo Electron Corp., United States) in radial and axial viewing configurations at a wavelength of 245.5 nm. Substrates and reaction products were analyzed on a Kristallyuks 4000 M chromatograph equipped with a flame ionization detector and a Petrocol® DH 50.2 capillary column coated with the polydimethylsiloxane stationary liquid phase (dimensions, 50 m  $\times$  0.25 mm; carrier gas, helium; split ratio, 1 : 90). Analysis conditions: column temperature, 235°C; detector temperature, 300°C; and injector temperature, 300°C. Chromatograms were recorded and analyzed on a computer using the program NetChrom. Conversion was calculated as a change in the relative surface areas of the substrate and products (%).

#### Catalyst Synthesis

The nanospherical mesoporous phenol-formaldehyde polymer NSMP was synthesized as described in [14]. For the synthesis of catalyst NSMP-Ru support NSMP (1.0 g) was suspended in water (90 mL) in a 25-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser, ruthenium(III) chloride (85 mg) was added, and the resulting mixture was stirred for 24 h. The solvent was removed on a rotor evaporator at 50°C. The residue was transferred into a 100-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser and suspended in a solution of ethyl alcohol (50 mL) and water (10 mL). NaBH<sub>4</sub> (0.15 g) was added in portions to the reaction mixture, and the mixture was stirred for 12 h at room temperature. The obtained suspension was centrifuged, and the catalyst was washed several times with water and ethyl alcohol and dried in air.



Fig. 1. CP/MAS <sup>13</sup>C and <sup>1</sup>H NMR spectra of the NSMP sample.

#### Catalytic Testing Procedure

A steel thermostated autoclave equipped with an insertable glass tube and a magnetic stirrer was loaded with the calculated amounts of the catalyst, substrate, and solvent. The autoclave was pressurized, filled with hydrogen to a pressure of 5.0 MPa, and held at a temperature of 200–250°C for 2 h under vigorous stirring. When the reaction was completed, the autoclave was cooled below room temperature and depressurized. The reaction mixture was analyzed by gas-liquid chromatography. Catalytic activity (TOF) for each reaction was calculated as the amount of the reacted substrate per mol of metal on the surface of particles per time unit.

#### **RESULTS AND DISCUSSION**

#### Catalyst Synthesis

Mesoporous phenol-formaldehyde nanospheres NSMP were prepared under hydrothermal conditions using low-concentrated reactant solutions. The resulting polymer was characterized by CP/MAS <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy, low-temperature nitrogen adsorption, and TEM (Figs. 1, 2).

The NMR spectra of NSMP samples show signals typical of mesoporous phenol-formaldehyde polymers; this confirms that the polymer structure of the material is retained and the template is completely removed [7]. In the NMR spectrum the signals are considerably broadened because of a small relaxation time in solids. In the <sup>1</sup>H NMR spectrum of the samples there are signals at 7.5 and 1.65 ppm. The first signal corresponds to aromatic protons, and the second signal is due to aliphatic protons of the CH<sub>2</sub> group. In the <sup>13</sup>C NMR spectrum there are three signals at 27, 128.5, and 154.5 ppm: the first signal is due to the carbon of the bridging CH<sub>2</sub> group, the signal at 128.5 ppm corresponds to the carbon of the aromatic ring, and



Fig. 2. (a, b) TEM images of the NSMP sample and (c) size distribution of nanospheres.

the signal at 154.5 ppm corresponds to the carbon of the aromatic moiety linked to the OH group.

The TEM images of the sample (Fig. 2) clearly show mesoporous channels typical of such materials. The statistical estimation of sizes for more than 500 nanospherical particles revealed that the size of nanospheres is within 60-320 nm and their average size is  $151 \pm 39$  nm.

In accordance with low-temperature nitrogen adsorption, the characteristics of the synthesized polymer are as follows: specific surface area,  $309 \text{ m}^2/\text{g}$ ; pore size, 3.9 nm; and pore volume, 0.16 cm<sup>3</sup>/g. According to the adsorption isotherm (Fig. 3), it can be assumed that the material contains small pores with sizes at the microporosity/mesoporosity boundary. This implies that a rise of the adsorption curve is observed in the range of low  $P/P^0$  values (0.05–0.1). which is inherent of microporous materials, whereas the hysteresis loop appearing owing to capillary condensation in material pores acquires the H-4-type mode, as is characteristic of micro-mesoporous carbons and mesoporous zeolites [15]. It should be emphasized that the desorption branch cannot form the closed curve at low relative pressures, which is typical of isotherms of porous polymers [16].

The catalyst was synthesized by impregnating the mesoporous polymer NSMP with the calculated amount of a RuCl<sub>3</sub> aqueous solution followed by reduction with NaBH<sub>4</sub>. The synthesized catalyst NSMP-Ru with a nominal ruthenium content of 4% was investigated by ICP-AES, TEM, and XPS.

As is clear from the microimages of the catalyst, Ru nanoparticles are situated predominantly in support pores (Fig. 4). It is found that the average size of Ru nanoparticles is  $1.4 \pm 0.5$  nm, which conforms to the characteristics of support pores. According to ICP-AES, the content of ruthenium is 3.6 wt %.

As evidenced by XPS studies (Table 1, Fig. 5), ruthenium in the synthesized catalysts occurs both in the zero-valence state (Ru<sup>0</sup>) and in the oxidized states  $(RuO_2, RuO_x)$  [17], whereas no RuCl<sub>3</sub> is detected. This indicates that the initial RuCl<sub>3</sub> is reduced completely. The presence of  $RuO_2$  may be explained by a high affinity of ruthenium for oxygen [18] and the subsequent oxidation of its surface during storage and analysis. The oxidized form  $RuO_x$  can result from interaction between Ru atoms with phenolic and carboxyl groups present on the polymer surface.

### Catalytic Experiments

In guaiacol hydrogenation the dependence of NSMP-Ru catalyst activity on solvent nature was studied. Systems water, *n*-dodecane, and water: *n*-dodecane were used as solvents (Table 2). As expected, the efficiency of the hydrogenation reaction in *n*-dodecane was lower, because, as is known, when phenol hydrogenation is carried out in aqueous medium water can in situ generate H<sup>+</sup> for further deoxygenation of oxygen-containing groups [19]; this contributes to the reaction acceleration. However, the guaiacol hydrodeoxygenation was the most effective in



Fig. 3. Nitrogen adsorption-desorption isotherm of the NSMP sample.

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Fig. 4. (a) Micrograph and (b) size distribution of nanoparticles of the catalyst NSMP-Ru.

the two-phase system water-n-dodecane. An increase in efficiency in the case of the two-phase system is probably related to a rapid transition of the formed products to the organic phase, whereas the substrate transformation proceeds in the aqueous phase.

A high degree of phenol hydrodeoxygenation is attained using mixed catalysts composed of a transition-metal-based catalyst and an acidic catalyst [20– 22] or bifunctional catalysts [23, 24]. It is also known that the selective guaiacol conversion to cyclohexanol can be reached with the use of basic compounds, for example, sodium hydroxide or magnesium oxide [25]. The reaction of guaiacol hydrogenation was studied in the presence of the NSMP-Ru catalyst and acidic or basic additives (Table 3).

Addition of a small amount of orthophosphoric acid (1 wt %) had no effect on the reaction, and methoxycyclohexanol was the key product. As the concentration of orthophosphoric acid was increased to 19.2 wt %, methoxycyclohexanol predominated in reaction products; however, they also contained cyclohexanediol, cyclopentanone, and C<sub>6</sub>-compounds: cyclohexane, benzene, and cyclohexene. This is evidence for the occurrence of hydrodeoxygenation processes. When sulfuric acid was added to the catalytic system, the degree of guaiacol hydrodeoxygen-

Parameters	C1s				Ru3 <i>d</i> <sub>5/2</sub>				Proportion of C1s in the C1s + Ru3d
	4	5	6	7	1	2	3	S	spectrum
Binding energy, $E_{\rm b}$ , eV	284.7	286.4	288.3	291.2	280.0	280.8	281.8	282.7	71%
Full width at half maxi- mum, FWHM, eV	1.6	1.6	2.1	3.6	1.0	1.4	1.3	2.0	
%	52	25	16	7	27	37	18	18	

Table 1. Approximation parameters of C1s + Ru3d spectra and the proportion of C1s



**Fig. 5.** Deconvolution of the C1*s* + Ru3*d* XPS spectrum of the catalyst NSMP-Ru. (*1-1*') Doublet of metallic ruthenium, (*2-2*') doublet of RuO<sub>2</sub>, (*ss*') satellites of doublet 2-2', (*3-3*') doublet of RuO<sub>x</sub>, (*4*) aromatic carbon, (*5*) C–OH group, (*6*) C=O group, and (*7*) shake-up satellite of the aromatic carbon.

ation increased and cyclohexanol, cyclohexanediol, and cyclopentanone became the key products; selectivity for C<sub>6</sub> products was 4%. When the reaction was conducted in the presence of sodium hydroxide, the guaiacol conversion decreased to 87% and the selectivity for compounds containing one oxygen atom was 13% higher than that without additives, whereas the addition of magnesium oxide did not cause considerable changes. Hence, basic compounds insignificantly influenced the guaiacol hydrogenation-hydrodeoxygenation reaction under the given conditions. If Sc(OTf)<sub>3</sub> was added to the system the degree of hydrodeoxygenation markedly increased only when temperature was increased to  $250^{\circ}$ C; this corresponded to the occurrence of guaiacol C–O bond hydrogenolysis in water at this temperature in the presence of the Lewis acid [26]. For example, selectivity for products containing one oxygen-containing group was 86% and selectivity for C<sub>6</sub> products increased to 12%.

Thus, we examined the effect of solvent and catalytic additives on the guaiacol hydrogenation in the presence of the catalyst based on ruthenium nanoparticles immobilized in nanospherical mesoporous phenol-formaldehyde polymer pores. It is shown that the hydrodeoxygenation of guaiacol is the most effective

Solvent	Conversion, %	TOF, $min^{-1}$	Selectivity, %
H <sub>2</sub> O	>99	116	Methoxycyclohexanol, 86 Cyclohexanol, 13 Methylcyclohexanol, <1
<i>n</i> -Dodecane	77	90	Methoxycyclohexanol, 78 Cyclohexanone, 2 Cyclohexanol, 17 C <sub>6</sub> -products, 3
H <sub>2</sub> O/ <i>n</i> -dodecane	100	117	Methoxycyclohexanol, 67 Methoxycyclohexane, 1 Cyclohexanol, 21 Cyclohexane, 5 Cyclohexanediol, 6

**Table 2.** Results of catalytic experiments on guaiacol hydrogenation over the NSMP-Ru catalyst in various solvents. Reaction conditions: v(guaiacol)/v(Ru) = 221 mol/mol, 0.4 mmol of guaiacol, 5.0 MPa of H<sub>2</sub>, 200°C, 2 h, and 1 mL of solvent

Table 3. Guaiacol hydrogenation over the catalyst NSMP-Ru in the presence of various additives. Reaction co	onditions:
$v(subs)/v(Ru) = 221 \text{ mol/mol}, 0.4 \text{ mmol of guaiacol}, 50 \text{ atm of } H_2, 200^{\circ}C (*250^{\circ}C), 2 \text{ h}, \text{ and } 1 \text{ mL of } H_2O$	

Additive	Conversion, %	TOF, $min^{-1}$	Selectivity, %
_	>99	116	Methoxycyclohexanol, 86 Cyclohexanol, 13 Methylcyclohexanol, <1
2.6 $\mu$ L of H <sub>3</sub> PO <sub>4</sub> (1 wt %)	>99	116	Methoxycyclohexanol, 85 Cyclohexanol, 14 Cyclohexanone, <1
50 $\mu$ L of H <sub>3</sub> PO <sub>4</sub> (ac)	98	114	Methoxycyclohexanol, 82 Cyclohexanol, 5 Cyclohexanediol, 4 Cyclopentanone, 6 C <sub>6</sub> products, 2
50 $\mu$ L of H <sub>2</sub> SO <sub>4</sub> (ac)	90	105	Methoxycyclohexanol, 21 Methoxycyclohexanone, 7 Cyclohexanol, 37 Cyclopentanone, 12 Cyclohexanediol, 19 C <sub>6</sub> -products, 4
4 mg of NaOH (0.1 mmol)	87	102	Methoxycyclohexanol, 73 Cyclohexanol, 27
50 mg of MgO	100	73	Methoxycyclohexanol, 89 Methoxycyclohexanone, <1 Cyclohexanone, <1 Cyclohexanol, 10
10 mg of Sc(OTf) <sub>3</sub>	100	58	Methoxycyclohexanol, 90 Cyclohexanol, 7 Cyclopentanol, 2 C <sub>6</sub> -products, <1
10 mg of Sc(OTf) <sub>3</sub> *	70	20	Methoxycyclohexanol, 2 Cyclohexanone, 63 Cyclohexanol, 6 Cyclopentanol, 13 Anisol, 4 Cyclohexane, 9 Benzene, 2 Cyclohexene, <1

when scandium(III) triflate is added to the system and the reaction is carried out at 250°C.

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## CONFLICT OF INTEREST

A.L. Maximov is the editor-in-chief of the journal *Petroleum Chemistry*. E. A. Karakhanov is a member of the editorial board of this journal. Other authors declare that there is no conflict of interest.

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