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Water-Assisted Selective Hydrodeoxygenation of Lignin-Derived Guaiacol to Monooxygenates

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Water, which frequently inhibits organic reactions, improves the hydrodeoxygenation activity of lignin-derived guaiacol on a bifunctional catalyst of Rh/SiO_2–Al_2O_3 in a biphasic mixture of *n*-decane and water. The unique properties of subcritical water appear to promote hydrodeoxygenation, which improves the production of monooxygenates by removing more oxygen atoms of guaiacol while suppressing the formation of fully deoxygenated hydrocarbons because of the poor solubility of hydrophobic monooxygenates.

Introduction

Water is a frequently used solvent, reagent, or product in biomass conversion processes,[1] including the fractionation, saccharification,[2] and fermentation[3] of lignocellulose. As significantly large amount of water is used during the chemical or biological conversion of carbohydrates, recent efforts to produce petroleum-like hydrocarbon fuels from biomass by the upgrading of thermochemically prepared bio-oil have frequently be hampered by the disadvantageous effects of water in reactants or products, including steam-induced high pressure, the creation of corrosive aqueous solutions, and the deactivation of catalysts.[4] Given the abundant oxygen functionalities in raw biomass, prepared bio-oil contains a considerable amount of water which is produced by the conversion of the oxygen atoms in the biomass. The thermochemical degradation of lignin produces pyrolysis oil, which is composed of water (20–30 wt%) and aromatic compounds containing oxygen functionalities of alcohols, ketones, esters, and ethers.[5] Aromatic oxygenates can be upgraded further to petroleum-like fuels and chemicals by hydrotreatment processes, particularly hydrodeoxygenation (HDO) as in this study, in which water must be appropriately handled to ensure the highest efficiency of HDO to produce high-quality hydrocarbon fuels including gasoline, diesel, and jet fuel.[6]

The reaction rate of hydrophobic organic compounds can be accelerated by water in a biphasic system containing hydrophilic and hydrophobic layers.[7] This type of water-mediated reaction can induce hydrophobic interactions[7b,8] and improve hydrogen bonding in the transition state,[9] leading to proton transfer. Many reports have attempted to demonstrate that these proton transfers proceed by the Grotthuss mechanism,[10] which has been performed via computer simulation,[11] scanning tunneling microscopy,[12] and spectroscopy methods including X-ray photoelectron spectroscopy,[13] IR[14] and NMR spectroscopy,[15] combined thermodynamic and kinetic analyses,[16] or in kinetic isotope effect studies.[17]

The goal of the present study was to elucidate the effects of water on the HDO of lignin-derived phenolic compounds, guaiacol in this study, as we previously observed the effects of carbohydrates.[18] Simulating the biphasic nature of thermochemically prepared bio-oils, a mixture of *n*-decane and water was used as a reaction medium for the hydrodeoxygenation of guaiacol. Although the effects of water are discussed briefly in the literature,[19] detailed modifications of HDO have not been studied. We investigated how the addition of water adjusts the HDO of lignin derivatives. The reaction pathway based on the results of this study is also suggested and a modification of the reaction pathway by the addition of water is discussed. Because of the required reaction temperature and the amount of H_2 gas for deoxygenation, the reaction conditions selected in this study were close to those of subcritical water, which reportedly improves the HDO activity.[6c,20] Possible monooxygenates, including cyclohexanol and cyclohexanone, selectively produced from lignin-derived phenolic compounds are precur-

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sors of the mass production of adipic acid and caprolactam to manufacture polymers including Nylon-6,6 and Nylon-6.[21]

Results and Discussion

Characterization of catalysts

Prior to catalysis, silica–alumina aerogel support (SAA-33, Al/(Si + Al) = 0.33 mol mol^{-1}) and SAA-33-supported Rh (Rh/SAA-33, 2.3 wt% Rh) were characterized by using N_2 physisorption, CO and H_2 chemisorption, high-angle annular dark field scanning transmission electron microscopy (HAADF–STEM), and NH_3 temperature-programmed desorption (NH_3-TPD). N_2 physisorption experiments revealed the decreasing BET surface area with possible destruction of the mesopores of SAA-33 during the impregnation of Rh and a subsequent calcination/reduction step (Supporting Information, Figure S1 and Table S1), but Rh/SAA-33 still contained 6 nm mesopores. The CO and H_2 chemisorption results (Tables S2 and S3) exhibited dispersions of 0.6 and 0.7, respectively, indicating the formation of highly dispersed Rh nanoparticles on the aerogel support (Table S4), as confirmed with HAADF–STEM (Figure S2). Based on observations of the HDO-determining acidity,[22] the acid sites on the catalysts were measured using NH_3-TPD (Table S5), which exhibited almost the same amounts of acid sites for Rh/SAA-33 and SAA-33 despite the fact that the strong acidity of SAA-33 was converted to weaker acidity on Rh/SAA-33 most likely because of the change of pore structures and the addition of Rh (Figure S3 and Table S6). Types of acid sites were further analyzed using pyridine FT-IR, which exhibited the preferred formation of Brønsted acid sites on Rh/SAA-33 (Figure S4 and Table S7).

Hydrodeoxygenation of guaiacol in a biphasic system

The biphasic system, composed of *n*-decane and water, affected the catalytic activity and selectivity of the hydrodeoxygenation (HDO) of guaiacol (GUA) (Figure 1 and Figure S7). The HDO of GUA (GUA–HDO) occurred in both the hydrophobic *n*-decane layer and the hydrophilic aqueous layer, but in different manners. If the water fraction, which is the molar ratio water/(water + *n*-decane), was less than 0.81, the addition of water appeared to suppress the conversion (or noble-metal-catalyzed hydrogenation) of GUA. The selectivity to compounds containing zero oxygen atoms (none-Os) decreased if the water was added to the reaction (0.088 < water fraction < 1.0). Interestingly, increasing the water fraction from 0.74 to 0.88, increased the conversion of GUA and the degree of deoxygenation [DOD = {(number of oxygen atoms removed)/(initial number of oxygen atoms in GUA)}/(conversion of GUA)], exhibiting values that were nearly identical to those of a water-free reaction system (water fraction = 0.0, Figure 1). The large DOD of the water-rich system was attributed to the high yield of compounds containing one oxygen atom (1-Os) despite the low yield of the none-Os. One can surmise that the hydrogen atoms or protons were supplied from the water, but the reaction without H_2 gas exhibited almost no deoxygenation regardless whether water existed or not (Figure S8). The low selectivity to none-Os during GUA–HDO in the biphasic system (BS–GUA–HDO) can be attributed to the addition of water. Water can donate a proton or a hydroxide ion, which creates a Lewis acid co-catalyst on the solid acid catalyst, Rh/SAA-33 in this study.[6c, 12b] The hydrolyzed protons from water and the pressurized H_2 gas can become involved in the removal of methoxy and hydroxyl groups from GUA molecules, which improves the removal of oxygen functionalities during the HDO reaction. The selectivity to 1-Os, including cyclohexanone and cyclohexanol, increased whereas those for none-Os, cyclohexane and methylcyclopentane in this case, decreased.

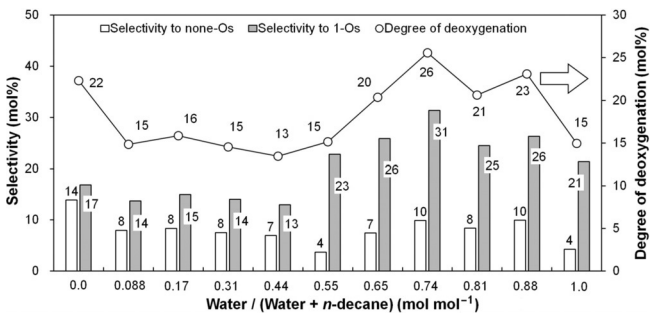

Figure 1. Effects of the water fraction on BS–GUA–HDO.

Rh/SAA-33 underwent the rearrangement of its surface structure in a water-rich environment leading to deactivation, as observed with TEM, XRD, and thermogravimetric (TG) measurements of the spent Rh/SAA-33 (Figure S2, S5, and S6). The TEM images exhibited Rh particles larger than 10 nm and wire-like silica–alumina (Figure S2). The possible leaching of alumina from the support was also observed if the water fraction was 1.0, which may be responsible for the rearrangement of the Rh particles and surface alumina structures. The XRD results exhibited the sintering of Rh particles and the formation of crystalline alumina and aluminum with an increase in the water fraction (Figure S5) because of the water-initiated rearrangement of the surface structure. TG exhibited significant carbon deposition if the water fraction was high (> 0.65), although this amount was less than 5% of the initial guaiacol reactant (Figure S6).

Thermal effects on GUA–HDO in a biphasic system

BS–GUA–HDO was performed at different temperatures (220–280 °C) to observe if water-mediated thermal activation occurred (Figure 2 and S9). The conversion of GUA in the biphasic system was less than that in the monophasic system (*n*-decane), and it decreased with an increase in the reaction temperature. The selectivity to compounds containing two oxygen atoms (2-Os) decreased with increasing temperature at a water fraction of 0.0, whereas that of 1-Os increased. The DOD in the biphasic system did not change significantly with an increase in the temperature despite the fact that the selectivities to none-Os and 1-Os changed. These observations can be attributed to the predominant deoxygenation and recombinations (or ring openings) at high temperatures rather than to hydro-

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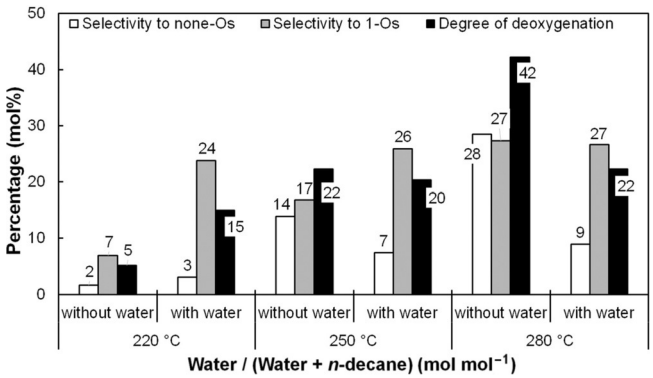

Figure 2. Effects of the reaction temperature on BS–GUA–HDO.

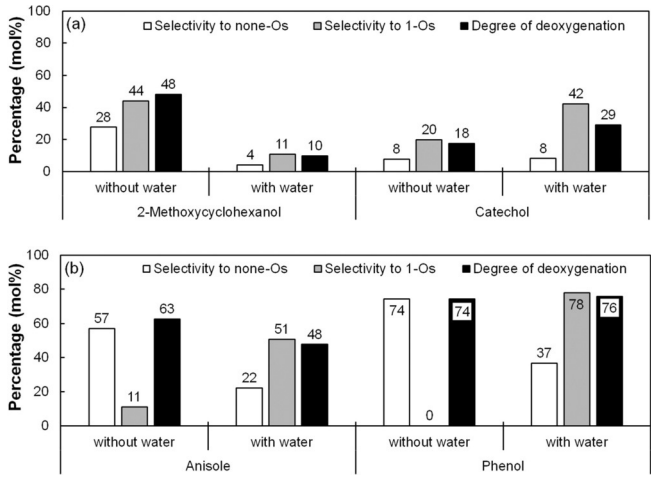

Figure 3. Conversion and degree of deoxygenation for the HDO of the intermediates: a) 2-methoxycyclohexanol and catechol, and b) anisole and phenol. The amount of catalyst was 20 mg, the reaction time was 0.5 h, and the concentration of the reactants was 0.2 M. The water fractions were 0.0 and 0.65 for the systems without water and with water, respectively.

genation. The high reaction temperature improved the deoxygenation and recombination rate, producing bicyclic and tricyclic compounds, including bicyclic alcohols and ketones. For example, a large amount of cyclohexylcyclohexanone was produced by the condensation of phenol, cyclohexanone, or cyclohexanol at 280 °C on Rh/SAA-33.[23] These observations are attributable to the improved hydrodeoxygenation at higher temperatures,[6c] at which the amount of hydrogen adsorbed on the metal catalyst increased, improving the hydrogenation activity and then the hydrodeoxygenation of saturated cyclic compounds.[24]

Product distribution of guaiacol hydrodeoxygenation in a biphasic system

Given the above observations of high selectivities to 2-methoyxcyclohexanol (2-Os), it appeared that the hydrogenation (saturation of phenyl ring) of GUA to form 2-methoxycyclohexanol occurred more readily than the HDO of 2-methoxycyclohexanol regardless whether water was present or not (Figure 3, S10, and S11(p)). The reaction barrier for the HDO of 2-methoxycyclohexanol, however, appeared to decrease as the water fraction increased, which increased the selectivity to 1-Os, including cyclohexanol and cyclohexanone obtained from 2-methoxycyclohexanol, if the water fraction exceeded 0.55. Because HDO occurred more readily for 2-methoxycyclohexanol to 1-Os in the biphasic system (BS) compared to the water-free system, the DOD increased despite the lower selectivity to the none-Os in the biphasic system compared to that in the water-free system. Note that cyclohexanol and cyclohexanone were the most abundant 1-Os (Figure S11 (g)–(m)). The selectivities to cyclopentanecarboxaldehyde and cyclopentanemethanol, both of which were formed from cyclohexanediol, increased if the water fraction was 0.65–0.74 and 1.0, respectively. The selectivity to anisole also increased when the water fraction was 0.55–0.88 during the GUA–HDO process.

Hydrodeoxygenation of oxygenated products in a biphasic system

In an effort to elucidate the effects of water on the catalysis of GUA, the HDO of possible intermediates, in this case, 2-methoxycyclohexanol, 1,2-dihydroxybenzene (catechol), anisole, and phenol, of the GUA–HDO was performed with the result that the addition of water appeared to suppress the deoxygenation of 1-Os but improve that of 2-Os (Figure 3, Figure S10 and S12):

(i) The conversion of methoxy functionalities was more difficult than that of hydroxyls for both water-free and BS–HDOs, which may be the rate-determining step of the GUA–HDO process. The HDO of 2-methoxycyclohexanol (2-O) produced 2-methoxycyclohexane (12.7% selectivity) for the water-free HDO and 2-methoxycyclohexanone (39.2% selectivity) for the BS–HDO (Figure S12 (a)).

(ii) The difficult conversion of methoxy functionalities was confirmed with the HDO of anisole (1-O). The selectivity to methoxycyclohexane was highest (10% for the water-free HDO and 30% for BS–HDO) (Figure S12 (b)). For the HDO of GUA and other compounds, the conversion of methoxy groups was more difficult than that of hydroxyls.

(iii) The HDO of catechol (2-O) exhibited high selectivity to cyclohexanone (28%) for the BS–HDO, which indicated that the addition of water improved the deoxygenation of 2-Os (2-hydroxycyclohexanone and 1,2-cyclohexandiol) and suppressed that of 1-Os (cyclohexanone) (Figure S12 (c)).

(iv) The HDO of phenol (1-O) exhibited high selectivity to cyclohexane (73%) for the water-free HDO and to cyclohexanol (67%) for the BS-HDO, which confirmed the suppressed deoxygenation of 1-Os (cyclohexanol) with the addition of water (Figure S12 (d)).

In addition to the effects of water, it is important to note that the removal of oxygen atoms was easier for 1-Os (anisole and phenol) than for 2-Os (2-methoxycyclohexanol and catechol) for both the water-free HDO and BS–HDO. The HDO of these compounds appeared to be affected by their functionalities (methoxy or hydroxyl), exhibiting larger DOD values for less complex reactants in the order of 2-methoxycyclohexa-

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nol < catechol < anisole < phenol. As the aromatic ring is a weaker nucleophile than hydroxyl or methoxy groups,[25] phenol can adsorb onto basic sites (nucleophile) in a nonplanar mode, producing cyclohexanone, or it can adsorb onto acidic site (electrophile) in a planar mode, predominantly producing cyclohexanol.[25–26] Anisole can produce cyclohexanone through hydrogenation followed by the demethylation of the adsorbed methoxy group, or it can produce methoxycyclohexane via the hydrogenation of the adsorbed aromatic ring on the catalyst surface.[19a,c] Direct hydrodeoxygenation can also occur by rapid dehydration after the hydrogenation of the aromatic ring.[19c]

Improved hydrodeoxygenation by the addition of water

Although the addition of water has been reported to suppress organic reactions by the deactivation of the catalysts,[4a,d,27] improved GUA–HDO in a biphasic mixture of *n*-decane and water has also been reported.[6c,19] The possible water-initiated adjustment of acid sites on the silica–alumina support was excluded based on the NH_3 TPD results (Figure S3 and Table S6) and the pyridine FTIR spectra (Figure S4 and Table S7) in this study. The addition of certain amounts of water improved the HDO exhibiting an increased yield of 1-Os compared to the water-free HDO. In addition to the water-involved improved hydrolysis, the water-assisted improved catalytic HDO activity can be attributed to the following causes:

(i) A proton transfer, most likely by the Grotthuss mechanism, may occur in a water-containing environment.[10,28] An aqueous catalytic reaction occurs upon the transfer of hydrogen on acid or base catalysts, by which water can be a proton donor or acceptor by interacting with reaction intermediates. In this system, hydrated ions (H_3O^+) may form as the active species, and the hydrated solid acid catalyst may have hydrated functionalities on the surface. Under these conditions, the proton transfer by the Grotthuss mechanism may occur on the solid acid catalyst, i.e., silica–alumina aerogel in this study. In this reaction system, guaiacol is saturated with H_2 at 50–150 °C prior to hydrodeoxygenation as reported previously.[22] Thus, 2-methoxycyclohexanol, a saturated form of guaiacol, is adsorbed onto the catalyst surface and converted to deoxygenated products (Figure S13). The acid sites on the catalyst surface were adjusted by the proton transfer via the Grotthuss mechanism (Figure S14–S16).

(ii) At high reaction temperatures, the self-dissociation constant of water increases, which supplies more protons to the reaction systems under H_2-rich environments. The improved acidity with better self-ionization (increased 630-fold from 10^{-14} at 25 °C to $10^{-11.2}$ at 250 °C) also improves the reaction.[6b,20,29]

(iii) The dielectric constants[6b,20,30] and viscosity[20] of water change at high temperature because of the rapid proton transfer of subcritical water.[6b,20] The improved solubility of organic reactants in the less polar (with a decreased dielectric constant from 78.5 F m^{-1} at 25 °C and 1 bar to 27.1 F m^{-1} at 250 °C and 50 bar) and less viscous (decreased viscosity from 0.89 MPa s at 25 °C to 0.11 MPa s at 250 °C) water may improve the HDO process.

Although the improved catalytic activity of oxygenates was observed, a lower production of none-Os with the selective production of 1-Os (cyclohexanol and cyclohexanone) was also observed. The incomplete deoxygenation can be attributed to the effects of water, which solvates the more hydrophobic 1-Os less compared to 2-Os, thus selectively producing 1-Os.

Suggested reaction pathways of the GUA–HDO

Based on the above results, we suggest that the GUA–HDO on Rh/SAA-33 occurs through four major paths: (i) the substitution of the methoxy or hydroxyl group of GUA to obtain 1,2-dimethoxybenzene or catechol followed by hydrogenation to yield 1,2-dimethoxycylcohexane or 1,2-cyclohexanediol, (ii) the hydrogenation of GUA to yield 2-methoxycyclohexanol, (iii) dehydration or demethanolation by the combination of hydroxyl and methoxy groups, and (iv) dehydration or demethanolation by the combination of catalyst-surface-adsorbed hydrogen and the hydroxyl group.[31] Although anisole can be converted to phenol by the substitution of a methoxy with hydroxyl group during hydrogenolysis,[6c,19c,32] the formation of phenol was not observed during the HDO of anisole in this study. The substitution and the elimination can be competitive reactions during GUA-HDO; however, elimination appeared to occur rather than substitution at a high temperature because of the high activation energy.[33]

Based on the suggested reaction pathways, the GUA–HDO of bifunctional catalysts composed of noble-metal (Rh) nanoparticles and solid acids (silica–alumina aerogel) is depicted in Scheme 1.[34] 2-Methoxycyclohexanone (c) or 2-methoxycyclohexanol (d) can be produced by the hydrogenation of GUA on a Rh surface onto which hydrogen atoms are dissociatively adsorbed. 2-Methoxycyclohexanone (c) and 2-methoxycyclohexanol (d) are further converted to methoxycyclohexane (h), cyclohexanone (i), cyclohexanol (j), and/or cyclohexane by partial hydrodeoxygenation. Hydroxyl from water can replace the methoxy group of 2-methoxycyclohexanol (d), producing 1,2-cyclohexanediol (f) at a low temperature during GUA–HDO in a biphasic system. Cyclopentanecarboxaldehyde (l) can be produced from cyclohexanediol (f) by means of pinacol rearrangement (Figure S17).[33,35] It can be further converted to cyclopentanemethanol (m) in an aqueous solution. In addition, 2-methoxycyclohexanol (d) and cyclohexanediol (f) can be converted to cyclohexanone (i) by intramolecular demethanolation and dehydration, respectively. The further conversion of cyclohexanone (i) and cyclopentanecarboxaldehyde (l) to fully deoxygenated compounds was more significant without water. Cyclohexene (k) was produced by the acid-catalyzed E1 elimination of cyclohexanol (j) (Figure S18).[33,35a]

Conclusions

Water in the subcritical phase can be a promoter of the bifunctional catalyst Rh/SAA-33. A proton transfer assisted by water may increase the hydrodeoxygenation activity, but in addition

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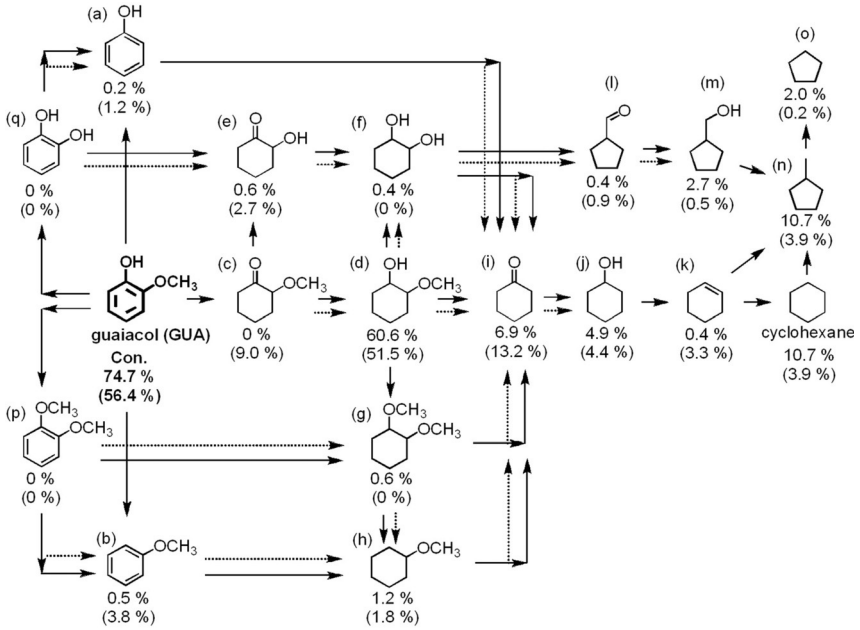

Scheme 1. Reaction pathway for BS–GUA–HDO. The solid arrow denotes the hydrophobic system and the dotted arrow represents the hydrophilic system. The values of the percentages refer to the GUA conversion and product selectivities without water (water fraction was 0) and, in parentheses, with water (water fraction was 0.65).

the unique properties of subcritical water, including a low dielectric constant, low viscosity, and a high self-ionization constant, also have fascinating implications if water is utilized during the hydrodeoxygenation process to upgrade lignocellulose-derived pyrolysis oil containing a significant amount of water to produce fuel-grade compounds (cyclohexanone, cyclohexanol, and cyclohexene). The selective formation of monooxygenates can also be used for the production of valuable chemicals, including cyclohexanol and cyclohexanone.

Experimental Section

Catalyst preparation

Silica–alumina aerogel (SAA-33, (Al)/(Si + Al) = 0.33 mol/mol) was prepared as previously described.[36] Rh (2.3 wt%) was impregnated onto the silica–alumina aerogel by the incipient wetness method. The catalysts were dried under an air flow at 120 °C for 12 h and reduced in a H_2 flow at 350 °C for 4 h prior to use.

Catalysis

The hydrodeoxygenation of guaiacol was conducted in a 160 mL Hastelloy C-276 batch reactor, which was filled with 0.448 M GUA in *n*-decane (40 mL; GUA, 2.3 g; *n*-decane, 27 g). 2.3 wt% Rh/SAA-33 (20 mg) was then added to the GUA solution. The reactor was filled with H_2 (40 bar) or He at RT and heated to 250 °C, at which temperature the reaction was performed for 85 min. The reactor was cooled to RT and the products were collected for further analysis. Water was added to observe its effects on the HDO of GUA (GUA–HDO): the (water)/(*n*-decane + water) or the water fraction was adjusted from 0.0 to 1.0 mol%. Specifically, the amounts of water added were 0.34, 0.72, 1.6, 2.7, 4.2, 6.4, 9.7, 15, 25, and 39 g in 0.45 M of GUA solution. The HDO of 0.20 M intermediates, in this case, 2-methoxycyclohexanol (reactant, 1.07 g; *n*-decane, 29 g); 1,2-dihydroxybenzene (catechol; reactant, 0.89 g, *n*-decane, 29 g of), anisole (reactant, 0.87 g, *n*-decane, 29 g), and phenol (reactant, 0.75 g, *n*-decane, 28 g) was studied using H_2 (40 bar at RT) and 2.3 wt% Rh/SAA-33 (20 mg) in a mixed solvent of *n*-decane (40 mL) at 250 °C for 30 min. BS–HDO reactions using intermediates were performed at (water)/(*n*-decane + water) = 0.65 using the amounts of 6.76 g of water for 2-methoxycyclohexanol, 6.88 g of water for catechol, 6.90 g of water for anisole, and 6.8 g of water for phenol. Products in the organic and aqueous phases were identified using a GC–MS (7890 A, Agilent Technologies) and were quantified using a GC–FID (YL6500 GC, Younglin), both of which were equipped with a HP-5 capillary column (60 m × 0.25 mm × 0.25 μm). The products derived from GUA were classified into three groups based on the number of oxygen atoms: none-Os, 1-Os, and 2-Os. The GUA conversion, product selectivity, product yield, and degree of deoxygenation (all in mol%) are defined in Equations (1)–(4):

$$\text{Conversion of GUA (mol\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

$$\text{Selectivity to products (mol\%)} = \frac{C_i}{C_0 - C_f} \times \frac{M_i}{M_0} \times 100 \quad (2)$$

$$\text{Yield of products (mol\%)} = \frac{C_i}{C_0} \times \frac{M_i}{M_0} \times 100 \quad (3)$$

$$\text{Degree of deoxygenation (mol\%)} = \frac{\sum\left(\text{yield (none-Os)} + \frac{\text{yield (1-Os)}}{2}\right)}{\text{conversion of GUA}} \quad (4)$$

in which C_0 and C_f are the initial and final amounts (mol) of GUA, respectively, C_i is the amount (mol) of the identified product, and M_0 and M_i are the numbers of moles of GUA and the product carbon atoms, respectively.

Characterization

The atomic compositions of the catalysts were measured by means of inductively coupled plasma atomic emission spectroscopy (ICP–AES; Polyscan-61E, Thermo Electron Corp., Winsford, Cheshire, UK), which was used to observe the (Al)/(Si + Al) = 0.33 mol mol^{-} and 2.3 wt% Rh loading. N_2 physisorption, CO and H_2 chemisorption, HAADF–STEM, XRD, TGA, NH_3-TPD, and pyridine FT-IR were performed as described in the Supporting Information.

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Keywords: biomass · biphasic catalysis · hydrogenation · rhodium · water

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