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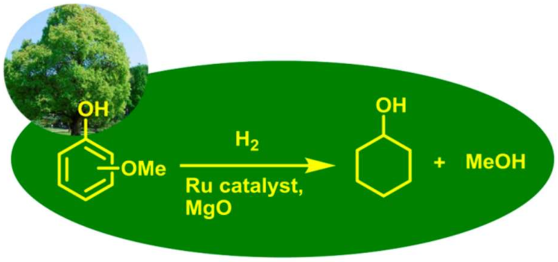
Methoxyphenols can be converted to cyclohexanol and methanol with H_2 over Ru/C combined with MgO.



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ARTICLE

Selective production of cyclohexanol and methanol from guaiacol over Ru catalyst combined with MgO

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Selective demethoxylation from aqueous guaiacol proceeded over Ru catalysts at relatively lower temperatures (≤433 K). Addition of MgO to the reaction media suppressed the unselective C-O dissociation. Cyclohexanol and methanol were obtained in high yield (>80%). A reaction route is proposed where partially hydrogenated guaiacol is decomposed into methanol and phenol, which is further hydrogenated to cyclohexanol.

Introduction

Much attention has been paid to the concept of biorefinery, where renewable biomass-related raw material is converted to valuable chemicals and fuel.[1-8] Since the oxygen content of biomass is usually much higher than common chemicals and transportation fuel, removal of oxygen with hydrogen (hydrodeoxygenation) is a key reaction in biorefinery. Furthermore, oxygen-containing chemicals are more attractive targets than hydrocarbon fuels because lower amount of hydrogen is necessary and the market price of products is higher, while selective partial hydrodeoxygenation to an oxygen-containing chemical is usually more difficult than total hydrodeoxygenation to hydrocarbons.[3,6] Guaiacol (2-methoxyphenol) is an important bio-related compound as one of components of bio-oil produced by fast pyrolysis of lignocellulose and as a model compound of lignin-derived monomers.[1,9-11] Hydrodeoxygenation of guaiacol has been studied using conventional hydrotreating catalysts such as CoMoS and NiMoS under severe conditions (typically ≥573 K).[12-14] Iron,[15,16] nickel,[17-19] cobalt,[20] rhenium,[21] tungsten,[22,23] molybdenum,[23,24] copper[25] and noble metal catalysts[17,24,26-33] have been also tested by several research groups using similar high reaction temperature. Reduction of guaiacol produces various compounds (Fig. 1). Total hydrodeoxygenation gives hydrocarbons (benzene and cyclohexane). Partial hydrodeoxygenation gives various oxygen-containing compounds: phenol, cyclohexanol, anisole and methoxycyclohexane. Demethylation reaction produces catechol and the hydrogenated compound 1,2-cyclohexanediol. The removed methoxy group is converted into methanol or methane. Simple hydrogenation of guaiacol can also proceed, producing 2-methoxycyclohexanol. Although there are some catalytic systems for production of hydrocarbons and methanol[17,27] or for production of phenol or cyclohexanol with good yields (<80%),[23-25,33] selective formation of both partial hydrodeoxygenation product and methanol has not been well established.[14] In this study, selective conversion of guaiacol to cyclohexanol and methanol was achieved by using Ru catalyst in basic conditions at relatively lower temperature. The selective removal of methanol from substrates with both hydroxy and methoxy groups may become one new route for the production of chemicals from lignocellulosic resources.

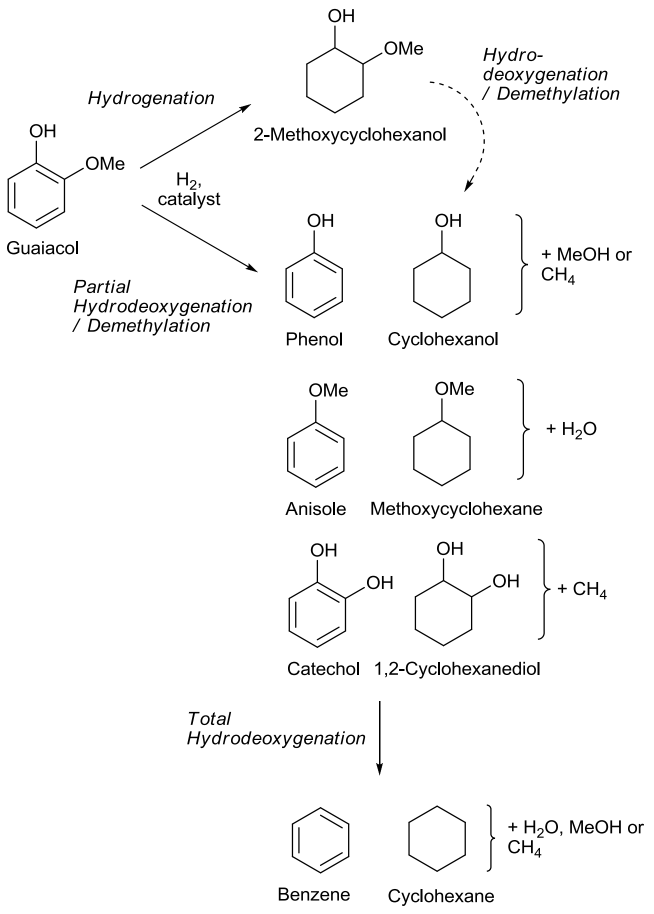


Fig. 1. Typical products of guaiacol reduction.

Results and discussion

Table 1. Reduction of guaiacol over various catalysts

Entry	Catalyst	Conv. (%)	Yield (%)[a]				Yield of C1 product (%)[b]	
			Cyclohexanol	2-Methoxycyclohexanol	Cyclohexane	Others	Methanol	Methane
1	Ru/C	>99	66	19	10	5	70	38
2	Rh/C	>99	36	26	12	Others 6, undetected[c] 18	66	12
3	Pd/C	82	1	43	1	2-Methoxycyclohexanone 33, others 4	5	<1
4	Pt/C	95	45	41	5	4	50	2
5	Ru/C + H-ZSM-5	>99	<1	6	46	Others 5, undetected[c] 44	69	40
6	Ru/C + MgO	98	79	12	7	1	85	3
7	Ru/C + NaOH	>99	77	18	4	2	76	2
8	Ru/MgO	98	78	14	3	2	83	<1

Reaction conditions: Guaiacol, 0.5 g; catalyst, 50 mg (5 wt% metal); additive, 50 mg (MgO or H-ZSM-5) or 1 mmol (NaOH); water, 10 g; H_2, 1.5 MPa; 433 K; 2 h. [a] Calculated based on the number of C6 rings. [b] Calculated based on the number of methoxy groups in the loaded substrate (i.e. [produced methanol or methane]/[loaded guaiacol] x 100 (%)). [c] Conversion (%) - (total yield of detected $\geq$C6 products (%)).

Optimization of catalysts

First, various carbon-supported noble metal catalysts were tested for the reduction of aqueous guaiacol with H_2 at 433 K in a batch reactor (Table 1, entries 1-4). Both hydrogenation and hydrodeoxygenation products were formed such as 2-methoxycyclohexanol, cyclohexanol and cyclohexane. The methoxy group that was removed in the formation of cyclohexanol was mainly observed as methanol. The highest yield of cyclohexanol was obtained over Ru/C catalyst (entry 1), although the formation of methane was significantly large. The total amount of methanol + methane + methoxy groups (guaiacol + 2-methoxycyclohexanol) in the reaction mixture over Ru/C was larger than that of loaded guaiacol (27% excess), and this is probably due to that methane was also formed by cracking reaction. Rh/C and Pt/C showed some activity in cyclohexanol formation; however, the selectivities to cyclohexanol were lower than that of Ru/C. Pd/C showed almost no activity in hydrodeoxygenation and the main products were hydrogenation products (2-methoxycyclohexanone and 2-methoxycyclohexanol). The Ru/C-catalyzed process was modified by addition of co-catalysts, and the results were also shown in Table 1 (entries 5-7). The pH values of the reaction mixture are shown in Table 2. The addition of acid promotes the total hydrodeoxygenation (entry 5), similarly to the previous studies.[27] The addition of base (MgO or NaOH) increased the yields of cyclohexanol and suppressed the methane formation (entries 6 and 7). The pH values before and after reaction (Table 2) confirmed that the reaction proceeded in basic conditions, while without base the reaction media was slightly acidic. The amount of C1 products + methoxy groups in the reaction mixture was almost the same as that of loaded guaiacol, indicating that addition of base suppressed the cracking reaction. We also prepared Ru/MgO catalyst by impregnation method and conducted the activity test. The dispersion of Ru determined by CO adsorption (CO/Ru) was similar for both Ru/C and Ru/MgO (0.44 and 0.36, respectively). Ru/MgO gave product distributions similar to those obtained by the Ru/C + MgO system (Entries 6 and 8). However, the Ru/MgO crumbled during the catalysis into mud, and the Ru particles were detached from the support and formed Ru black. We selected Ru/C + MgO as an optimum system because of the high performance and easy handling. It should be noted that the use of base in hydrodeoxygenation reactions is relatively rare, in comparison with the use of acid. One of rare examples of hydrodeoxygenation in basic conditions is selective formation of 1,2-propanediol from glycerol over metal catalysts.[34] However, the mechanism proposed for this reaction can be only applied to 1,3-disubstituted substrates: dehydrogenation to aldehyde (glyceraldehyde), removal of α-hydrogen and β-OH group as dehydration to conjugated aldehyde (2-hydroxyacrolein), and hydrogenation to product (1,2-propanediol). The mechanism of our system should be different from that of glycerol hydrodeoxygenation over metal + base catalysts.

Table 2. pH values of the reaction mixture

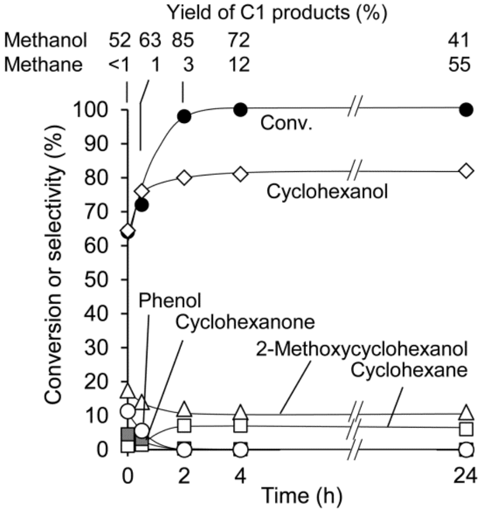
Components of the media	pH
Ru/C	6.0
Ru/C + H-ZSM-5	4.1
Ru/C + MgO	10.8
Ru/C + NaOH	13.0
Ru/MgO	10.7
Ru/C + MgO + guaiacol	8.9
Ru/C + MgO + guaiacol (after reaction)	9.9

The amount of each compound was the same as shown in Table 1.

Effect of reaction conditions

The time courses of reduction of guaiacol over Ru/C with or without MgO were shown in Fig. 2. The reaction proceeded to some extent during the heating to the reaction temperature. Over RuC + MgO (Fig. 2a), yields of cyclohexanol, 2-methoxycyclohexanol and cyclohexane were not changed after the guaiacol conversion reached 100%. Hydrogenolysis of methanol to methane gradually proceeded, and the selectivity to methanol based on the converted methoxy group (= conversion – yield of 2-methoxycyclohexanol) was decreased from >95% (2 h) to 46% (24 h). Good yield of cyclohexanol and methanol was obtained at 2 h. Phenol and cyclohexanone were detected at short reaction time, suggesting that these compounds were the intermediates of cyclohexanol formation. The time course was more complex in the case without MgO (Fig. 2b). In the initial stage, the main products were cyclohexanol, 2-methoxycyclohexanol and phenol, similarly to the case in the presence of MgO, although the selectivity to cyclohexanol was lower. Selectivities to cyclohexanol and 2-methoxycyclohexanol were decreased after the guaiacol conversion reached 100%. Large amounts of cyclohexane and methane were formed at long reaction time, and methanol was almost completely consumed after 24 h. Formation of 1,2-cyclohexanediol was also characteristic to the case without MgO. The selectivity to 1,2-cyclohexanediol increased at first, indicating that 1,2-cyclohexanediol was the product of consecutive reactions. Among the products observed in the initial stage, 2-methoxycyclohexanol can be the direct source of 1,2-cyclohexanediol. The yield of 1,2-cyclohexanediol decreased at long reaction time, probably because of the hydrodeoxygenation to cyclohexanol and eventually cyclohexane. Anyway, without MgO the hydrodeoxygenation of saturated compounds can proceed over Ru/C. Yield of cyclohexanol over Ru/C alone was always lower than that over Ru/C + MgO.

(a) Ru/C + MgO



(b) Ru/C only

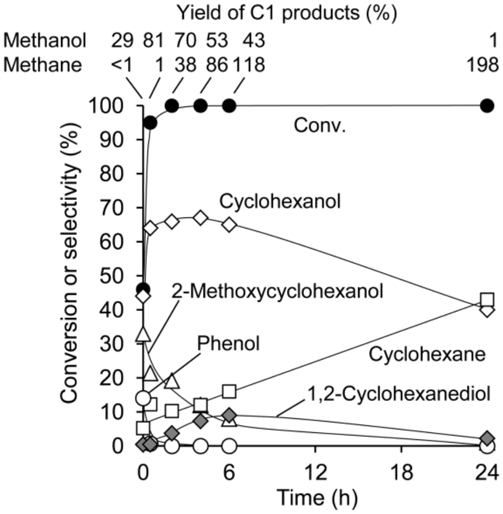


Fig. 2. Time courses of reduction of guaiacol over Ru/C + MgO (a) and only Ru/C (b). Conditions: Guaiacol, 0.5 g; Ru/C, 50 mg; MgO, 0 or 50 mg; water, 10 g; H_2, 1.5 MPa; 433 K. Selectivities to products not shown in the graph were always lower than 1%.

We investigated the dependences of selectivity of Ru/C + MgO system on the reaction parameters (Fig. 3). Although the conversion of guaiacol was very high in these data, the selectivity patterns can be directly compared because reactions of cyclohexanol, 2-methoxycyclohexanol or cyclohexane are very slow over Ru/C + MgO (Fig. 2a). Higher selectivity to cyclohexanol was obtained at higher reaction temperature under lower hydrogen pressure. 2-Methoxycyclohexanol formation was suppressed by these conditions, while cyclohexane formation was slightly enhanced by higher reaction temperature.

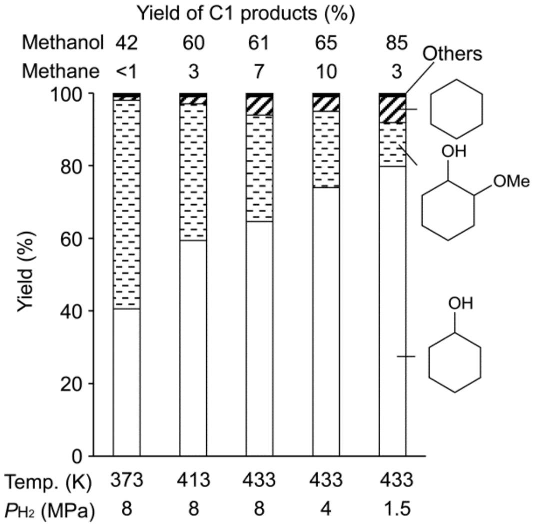


Fig. 3. Effect of reaction conditions in the reduction of guaiacol over Ru/C + MgO. Conditions: Guaiacol, 0.5 g; Ru/C, 50 mg; MgO, 50 mg; water, 10 g; 2 h.

The reuse experiment was conducted to see the stability of catalyst (Fig. 4). The used Ru/C and MgO was collected by filtration, washed with ethanol, dried, and reused for another catalytic run. The used catalysts showed good yield of cyclohexanol and methanol. However, the activity was slightly decreased by reuses, and significant amount of guaiacol (or products) disappeared from the reaction solution over used catalysts. During the catalysis, MgO powder was transformed into muddy material, probably $Mg(OH)_2$. The decreases of catalytic activity and material balance might be due to the reaction of guaiacol with $Mg(OH)_2$. With enough reaction time, the used catalyst can give almost the same yield of cyclohexanol and methanol as those obtained by fresh one, suggesting that trapping of guaiacol by $Mg(OH)_2$ is weak and reversible.

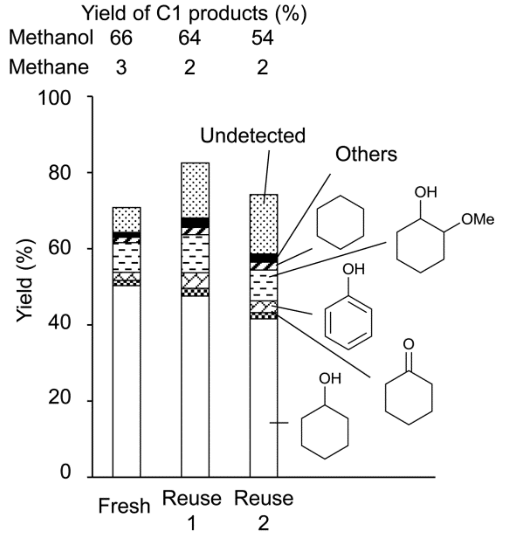


Fig. 4. Reuse experiments of Ru/C + MgO. Conditions: Guaiacol, 1 g; Ru/C, 100 mg; MgO, 100 mg; water, 10 g; H_2, 1.5 MPa; 433 K; 2 h. “Undetected” means the

loss of material balance: [(Loaded guaiacol (mol))-(Total detected ≥C6 products (mol))-(Unreacted guaiacol (mol))]/(Loaded guaiacol (mol)) x 100 (%).

Application to other methoxyphenols

The Ru/C + MgO system was applied to various related substrates (Table 3). Guaiacol and 3-methoxyphenol were converted to cyclohexanol in good yield. 4-Methoxyphenol was also converted to cyclohexanol although the yield was lower. The system can be also applied to 2,6-dimethoxyphenol, which is also an important motif in the bio-oil-based or lignin-based monomers[11]: both methoxy groups were removed and good cyclohexanol yield was obtained. For 1,2-dimethoxybenzene and anisole, which have only methoxy groups and no OH group, hydrogenation was the main reaction and the yields of hydrodeoxygenation products were low. Therefore, the Ru/C + MgO system is effective in the selective removal of methoxy group from phenolic substrates.

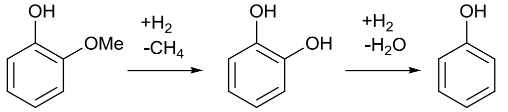
Table 3. Reduction of aromatics with methoxy groups over Ru/C + MgO

Substrate	Conv. (%)	Product (Yield (%)[a])	C1 product (Yield (%)[b])
Guaiacol	98	Cyclohexanol (79), 2-methoxycyclohexanol (12), cyclohexane (7), others (1)	Methanol (85), methane (3)
3-Methoxy-phenol	>99	Cyclohexanol (85), 3-methoxycyclohexanol (10), cyclohexane (4), others (1)	Methanol (85), methane (7)
4-Methoxy-phenol	>99	Cyclohexanol (55), 4-methoxycyclohexanol (41), cyclohexane (4), others (1)	Methanol (52), methane (8)
2,6-Dimethoxy phenol	>99	Cyclohexanol (69), 2-methoxycyclohexanol (16), cyclohexane (4), others (10)	Methanol (84), methane (5)
1,2-Dimethoxy-benzene	>99	1,2-Dimethoxycyclohexane (47), methoxycyclohexane (19), cyclohexane (16), cyclohexanone (9), cyclohexanol (7), 2-methoxycyclohexanol (3), others (<1)	Methanol (43), methane (9)
Anisole	>99	Methoxycyclohexane (69), cyclohexanol (21), cyclohexane (9)	Methanol (25), methane (14)

Reaction conditions: Substrate, 0.5 g; Ru/C, 50 mg; MgO, 50 mg; water, 10 g; H_2, 1.5 MPa; 433 K; 2 h. [a] Calculated based on the number of C6 rings. [b] Calculated based on the number of methoxy groups in the loaded substrate.

Reaction mechanism

In the literature several reaction routes have been proposed for the hydrodeoxygenation of guaiacol over noble metal catalysts to mono-functionalized products (phenol, cyclohexanone and cyclohexanol): Demethylation of guaiacol to catechol followed by hydrogenolysis (eqn (1)),[24,28,33] hydrogenation of guaiacol to 2-methoxycyclohexanol followed by hydrogenolysis to cyclohexanol (eqn (2))[31] and hydrogenation to 2-methoxycyclohexanone followed by hydrogenolysis to cyclohexanone (eqn (3)).[26,27,29] In the cases of non-noble-metal based catalysts, the mechanism involving demethoxylation of guaiacol has been proposed (eqn (4)), while the reaction route represented as eqn (1) is reported to be also involved in some systems.[14,15,21,24,25] Nimmanwudipong et al. reported that Pt/MgO catalyst can convert guaiacol to a mixture of phenol, catechol, cyclopentanone and other products at 573 K via various reaction routes including eqns (1) and (4).[30]



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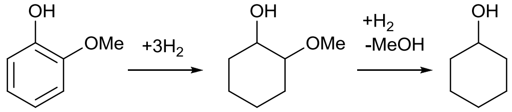

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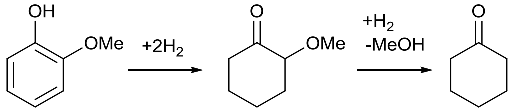

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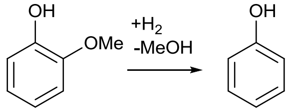


(4)

We investigate the reactivity of various substrates including possible intermediates to determine the reaction mechanism of Ru/C + MgO system (Table 4). Catechol, which is an intermediate in the reaction route of eqn (1), was less reactive than guaiacol over Ru/C + MgO (Entry 1), and the main product was 1,2-cyclohexanediol. Considering that catechol and 1,2-cyclohexanediol were not observed in the time course of guaiacol reduction over Ru/C + MgO (Fig. 2a), the reaction route of eqn (1) is not plausible. It should be also noted that methane was hardly formed at shorter reaction time. The reactivity of 2-methoxycyclohexanol was even lower (Entry 3). The time course shown in Fig. 2a also shows the low reactivity of 2-methoxycyclohexanol, indicating that 2-methoxycyclohexanol is not an intermediate of cyclohexanol formation; reaction route of eqn (2) is not plausible. The reactivity of 2-methoxycyclohexanol was slightly higher when used alone as a substrate than during guaiacol reduction. This phenomenon can be explained by the competitive reaction of methanol which can be adsorbed more strongly on the catalyst surface than 2-methoxycyclohexanol. Hydrogenation of phenol, which was observed at short reaction time in the reduction of guaiacol, was fast and produced cyclohexanol and small amount of cyclohexanone (Entry 5). Cyclohexanone was also observed at low conversion in the reduction of guaiacol (Figs. 2 and 4). These data suggest that phenol is an intermediate of the formation of cyclohexanol, agreeing with the reaction route of eqn (4). Phenol is more frequently observed product than cyclohexanol in the literature for guaiacol demethoxylation. The difference in the main product between our system and literature ones can be due to the difference in reaction temperature (433 K and ~573 K) and/or the difference in hydrogenation activity of catalysts. The reaction route of eqn (3) does not involve phenol as an intermediate and is not plausible in our case.

We also conducted the reactivity tests of the same substrates over Ru/C catalyst alone (Table 4, entries with even numbers). The activity of Ru/C alone was much higher in C-O dissociation of saturated alcohols such as cyclohexanol, 2-

Table 4. Reduction of various substrates over Ru/C + MgO or Ru/C alone

Entry	Substrate	Catalyst	Time (h)	Conv. (%)	Product (Yield (%)[a])	C1 product (Yield (%)[b])
1	Catechol	Ru/C+MgO	2	57	Cyclohexanol (14), 1,2-cyclohexanediol (40), cyclohexane (2), others (1)	-
2	Catechol	Ru/C	2	86	Cyclohexanol (39), 1,2-cyclohexanediol (39), cyclohexane (7), others (2)	-
3	2-Methoxy-cyclohexanol	Ru/C+MgO	2	8[c]	1,2-Cyclohexanediol (4), cyclohexanol (2), cyclohexane (2)	Methanol (1), methane (14)
4	2-Methoxy-cyclohexanol	Ru/C	2	36[c]	1,2-Cyclohexanediol (29), cyclohexanol (5), cyclohexane (1)	Methanol (3), methane (46)
5	Phenol	Ru/C+MgO	0.5	96	Cyclohexanol (89), cyclohexanone (4), others (2)	-
6	Phenol	Ru/C	0.5	>99	Cyclohexanol (95), cyclohexane (5), others (1)	-
7	Cyclohexanol	Ru/C+MgO	2	2	Cyclohexane (1), cracked products (1)	-
8	Cyclohexanol	Ru/C	2	11	Cyclohexane (5), cracked products (6)	-
9	Methanol[d]	Ru/C+MgO	2	16	-	Methane (16)
10	Methanol[d]	Ru/C	2	85	-	Methane (85)

Reaction conditions: Substrate, 0.5 g; Ru/C, 50 mg; MgO, 0 or 50 mg; water, 10 g; H_2, 1.5 MPa; 433 K. [a] Calculated based on the number of C6 rings. [b] Calculated based on the number of methoxy groups in the loaded substrate. [c] Trans-cis isomerization was excluded for calculation. [d] Methanol, 4 mmol.

methoxycyclohexanol and methanol than Ru/C + MgO. Therefore one role of MgO in the catalysis of Ru/C + MgO is the suppression of unselective C-O dissociation. Ru/C showed very high activity in phenol hydrogenation, as well as Ru/C + MgO. Phenol was detected at very short reaction time in guaiacol reduction over Ru/C (Fig. 2b), suggesting that the reaction route of eqn (4) was present in the system of Ru/C alone, while the route where 2-methoxycyclohexanol and 1,2-cyclohexanediol act as intermediates can proceed to some extent.

Demethoxylation of guaiacol to phenol and hydrogenation of guaiacol to 2-methoxycyclohexanol can simultaneously proceed, and the relative rate between these reactions affects the selectivity. Considering the higher selectivity to cyclohexanol and the absence of the reaction route from 2-methoxycyclohexanol to cyclohexanol in the presence of MgO, another role of MgO is to increase the relative rate of demethoxylation to phenol in comparison with hydrogenation to 2-methoxycyclohexanol.

Now we propose the reaction network of guaiacol reduction over Ru/C with or without MgO (Fig. 5). Demethoxylation of guaiacol to phenol consists of one hydrogen molecule and removal of one methanol. First guaiacol is partially hydrogenated to dihydroguaiacol. Two reactions can proceed from dihydroguaiacol: further hydrogenation to 2-methoxycyclohexanol and removal of methanol to phenol. The latter reaction constitutes demethoxylation of guaiacol (eqn (4)). Acidic phenolic compounds are stabilized by basic conditions, while saturated compounds such as 2-methoxycyclohexanol are not. This difference might increase relative rate of demethoxylation to hydrogenation. Higher temperature can also increase the relative rate of methanol removal, which increases the number of molecules, to hydrogenation, which decreases the number of molecules. Higher H_2 pressure promotes the hydrogenation of dihydroguaiacol, decreasing the relative rate of methanol removal. Phenol is readily hydrogenated to cyclohexanol over Ru/C regardless of whether MgO is added or not. Without MgO, further C-O dissociations can proceed over Ru/C. There is another route for cyclohexanol production over Ru/C: C-O dissociation of 2-methoxycyclohexanol. However, C-O dissociation of cyclohexanol in the absence of base much decreases the cyclohexanol yield. As a result, higher cyclohexanol yield can be obtained in the presence of MgO. In addition, methanol yield is enhanced by addition of MgO by suppression of C-O dissociation of methanol to methane.

The mechanism of C-O dissociation of saturated compounds

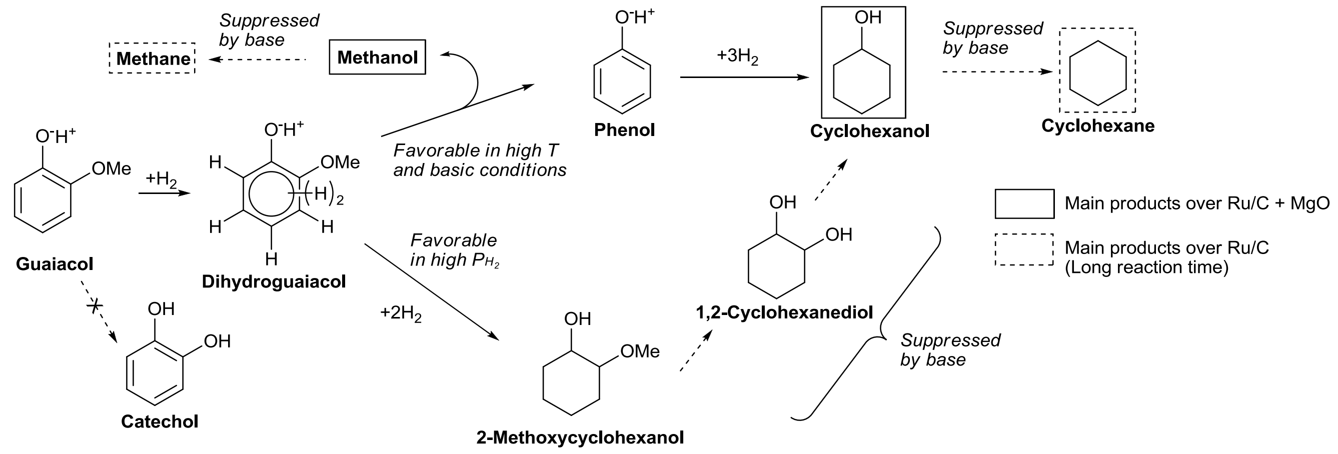
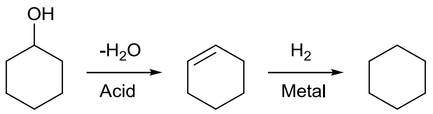


Fig. 5. Proposed reaction pathways of guaiacol reduction over Ru/C + MgO catalysts.

is not well known. The reaction route composed of acid-catalyzed dehydration to alkenes and subsequent hydrogenation has been proposed for hydrodeoxygenation of alcohols such as cyclohexanol over metal catalysts under acidic conditions (eqn (5)).[3,35-37] The dehydration + hydrogenation mechanism may be involved in this system and inhibited by the presence of base. However, the dehydration + hydrogenation mechanism cannot be applied to the formation of methane from methoxy group or methanol (Table 4, entries 4 and 10). Ruthenium catalysts are known to be very effective in methanation reaction (hydrogenation of carbon oxides to methane),[38] which property may be related to the methane formation in this system.



(5)

Conclusions

Ru catalyst combined with MgO can selectively convert methoxyphenols such as guaiacol into cyclohexanol and methanol with H_2 in relatively mild conditions. This reaction competes with hydrogenation to methoxycyclohexanols, and higher reaction temperature and lower hydrogen pressure conditions are favorable to the production of cyclohexanol. The reaction is suggested to proceed via the demethoxylation to phenol followed by hydrogenation to cyclohexanol. The presence of base suppresses the unselective C-O dissociation by Ru catalyst, and may also promote the demethoxylation step via stabilizing the produced phenol.

Acknowledgements

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Experimental section

Carbon-supported noble metal catalysts (5 wt% loading) were purchased from Wako. MgO-supported Ru catalyst (5 wt% Ru) was prepared by impregnation of MgO (UBE 500 A, calcined at 973 K for 1 h) with aqueous $Ru(NO)(NO_3)_3$ and subsequent heating under N_2 at 573 K for 2 h. XRD patterns were measured with Rigaku MiniFlex600 diffractometer. The amount of CO chemisorption was measured in a high-vacuum system using a volumetric method at room temperature. The samples for CO adsorption were treated with H_2 at 473 K just before measurement. Substrates were commercially available and used as received. The hydrodeoxygenation of guaiacol was performed in 190-ml stainless-steel autoclave with an inserted glass vessel. The noble-metal catalyst, co-catalyst (MgO; H-ZSM-5: JRC-Z5-90H(1), Süd-Chemie Catalysts and Catalysis Society of Japan, Si/Al_2=90), guaiacol (substrate), and water (solvent) were put into the autoclave together with a spinner. After sealing the reactor, the air content was purged by flushing three times with 1 MPa hydrogen (99.99%; Nippon Peroxide Co., Ltd.). The autoclave was then heated to the reaction temperature, and the temperature was monitored using a thermocouple inserted in the autoclave. The heating required about 40 min. The catalyst was reduced during the heating. Then the hydrogen pressure was increased to the intended value. After an appropriate reaction time, the reactor was cooled down and the gases were collected in a gas bag. The autoclave contents were diluted with ethanol and transferred to a vial, while the catalyst was separated by centrifugation and filtration. Analyses were conducted with GC and GC-MS with TC-WAX, InertCap 5MS/Sil, or Rtx-1-PONA capillary column. Yields were calculated based on the number of C6 rings in the reactant and products except for C1 products (methanol and methane). Yields of methanol and methane were calculated from the number of methoxy groups in the substrate. Yields of cracked products were calculated on the carbon basis.

Notes and references

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