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Short communication

Catalytic transfer hydrogenation/hydrogenolysis of guaiacol to cyclohexane over bimetallic RuRe/C catalysts

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ABSTRACT

The hydrodeoxygenation of lignin monomer guaiacol via catalytic transfer hydrogenation was studied with 2propanol as a hydrogen donor and Ru-based catalysts. Guaiacol was mainly converted into a partially deoxygenated product, cyclohexanol (>70% selectivity), over Ru/C catalysts with the hydrogen produced in-situ from 2propanol. An addition of Re to Ru/C catalysts significantly enhanced the rate of C—O hydrogenolysis, resulting in the complete deoxygenation to cyclohexane (~60% selectivity). The remarkable deoxygenation ability of the bimetallic RuRe/C catalyst is attributed to its bifunctional characteristic, by which Ru catalyzes the hydrogenation-hydrogenolysis of guaiacol and Re provides acid sites to promote cyclohexane production via hydrogenolysis.

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1. Introduction

Lignocellulosic biomass has been widely studied as a renewable feedstock for the production of fuels and chemicals. Fast pyrolysis is a promising technology to convert solid biomass into a liquid fuel called a bio-oil [1]. However, the fuel quality of the bio-oils is very low because they are highly oxygenated and are not compatible with the existing petroleum-derived oils [2]. Catalytic hydrodeoxygenation (HDO) is an effective method to convert bio-oils into high-grade fuels by selectively removing oxygen from bio-oils [3]. Therefore, many researchers have focused on the development of highly active and stable catalysts for the HDO of bio-oils.

Guaiacol is a representative bio-oil model compound because it contains two types of C—O bonds, hydroxyl (Csp₂OH) and methoxy (Csp₂OCH₃), which are prevalent in the phenolic compounds of biooils [4]. The HDO of guaiacol has been studied using a range of catalysts, including metal sulfides (NiMoS and CoMoS), noble metals (Pt, Rh), and non-noble transition metals (Ni, Fe) [3]. In general, noble metals such as Pt show higher HDO activity, but the undesired hydrogenation of the aromatic ring is favored, leading to high H₂ consumption. Combining metal sites with acid sites has been suggested as an effective means of enhancing the deoxygenation activity of catalysts [5–9]. The acid sites

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can be provided by either the support or added promoters. For instances, Lee et al. reported that Rh/silica-alumina is highly active for the hydrodeoxygenation of guaiacol due to the synergistic effect of metal-catalyzed hydrogenation and acid-catalyzed dehydration [6]. Wang et al. reported that the addition of Fe to Ni/SiO₂ substantially enhanced the deoxygenation activity of m-cresol [8].

In addition to catalyst development, the HDO conditions are an important issue because the HDO of bio-oils typically involves harsh reaction conditions, such as high temperatures (573–723 K) and high H_2 pressure, both of which increase the process costs. Catalytic transfer hydrogenation (CTH) is an efficient method for the reduction of carbonyl groups without using molecular H_2 at moderate temperatures [10]. Several groups have reported the effectiveness of the CTH process for reducing the oxygen content in a range of biomass-derived molecules, such as glycerol [11,12], levulinic acid [13,14], furfural [15–17] using secondary alcohols (e.g., 2-propanol) or formic acid as hydrogen donors. However, reports of the CTH of phenolic compounds such as guaiacol are scarce. There have been only limited studies using Raney Ni and Pd/C catalysts [18,19].

In this study, we investigate the catalytic transfer hydrogenation/ hydrogenolysis of guaiacol to cyclohexane using 2-propanol as a hydrogen donor over Ru-based catalysts. Ru shows activity superior to those of Ni and Pd for the dehydrogenation of 2-propanol and the hydrodeoxygenation of guaiacol. The Re promotion of the Ru/C catalysts further enhances the rate of C—O hydrogenolysis, resulting in high selectivity toward cyclohexane (~60%).





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2. Experimental

2.1. Catalyst preparation

5 wt% Ru/C and 10 wt% Ni/C catalysts were prepared by incipient wetness impregnation method. Activated charcoal was impregnated with aqueous solutions of RuCl₃·xH₂O and Ni(NO₃)₂·6H₂O, respectively. After drying at 383 K for 10 h, Ru/C and Ni/C were reduced at 573 K and at 673 K, respectively, in a flowing mixture of H_2 (5%) and N_2 (95%). 5 wt% Pd/C and 5 wt% Ru/Al₂O₃ catalysts were directly purchased from Sigma Aldrich and reduced at 573 K before reaction. Bimetallic RuRe/C catalysts were prepared by successive impregnation. 4 wt% Ru/C catalysts were prepared and dried at 378 K. The dried Ru/C catalysts were then impregnated with aqueous solution of NH₄ReO₄. The loading amount of Re was varied based on an atomic ratio (atomic ratio of Re/Ru = 0.25, 0.5, 0.75). For comparison, Re/C catalyst was also prepared by incipient wetness impregnation with aqueous solution of NH₄ReO₄. After impregnation, the catalysts were dried in air (383 K) and were reduced at 523 K in flowing H₂, 5 wt% Ru/H-BEA catalyst was prepared by impregnation of H-Beta zeolite (H-BEA, $SiO_2/Al_2O_3 = 38$, Zeolyst) with an aqueous solution of $RuCl_3 \cdot xH_2O$.

2.2. Characterization

CO-chemisorption was performed using a pulsed injection of 10% CO/He (50 sccm) with a BETCAT-B (BEL JAPAN) equipped with a thermal conductivity detector. The reducibility of Ru and Re metals was characterized by temperature programmed reduction (TPR) using a BETCAT-B. TPR was carried out under 5% H₂/Ar flow (30 sccm) from 303 K to 1173 K with a heating rate of 10 K/min. The TEM images were obtained with a FEI Talos F200X transmission electron microscopy (TEM). Energy dispersive X-ray spectroscopy (EDX) mapping analyses were also conducted using the same microscope to examine the detailed distribution of Ru and Re on the carbon support.

2.3. Catalytic experiments

Reactions were performed in a stainless steel 150 mL Parr reactor. For a typical reaction, 0.25 g of guaiacol (99%, Sigma Aldrich), 25 mL of 2-propanol (99.9%, Sigma Aldrich), and 0.1 g of the catalysts were charged in the reactor. The reactor was sealed and pressurized with N₂ to 2 MPa. The reactor was then heated up to 473–513 K using an electrical furnace and stirred at 300 ± 50 rpm with a gas entrainment impeller. After the designated reaction time, the liquid products were collected, filtered, and analyzed by means of a gas chromatography (Agilent 7890B) equipped with a flame ionization detector (FID).

3. Results and discussion

3.1. Catalyst screening for the CTH of guaiacol

Initial experiments focused on the investigation of the activity of several monometallic catalysts (Ni, Pd, and Ru) supported on carbon



Fig. 1. H_2 -TPR profiles of Ru/C, Re/C, and RuRe/C catalysts with Re/Ru atomic ratios of 0.25, 0.5, and 0.75. Before TPR measurements, the catalysts were treated under 5% O_2 /He flow at 403 K for 1 h.

for the CTH of guaiacol. Table 1 illustrates the conversion and product selectivity over different catalysts. The conversion of guaiacol decreased in the order Ru/C > Pd/C > Ni/C. Importantly, the conversion of 2propanol also decreased in the order Ru/C > Pd/C > Ni/C, implying that the rate of 2-propoanol dehydrogenation is closely related to the rate of CTH of guaiacol. Ni/C exhibited significantly lower conversion of guaiacol (17%) than those of Ru/C (99%) and Pd/C (90%), respectively. This could be due to the lower Ni dispersion (0.98%) and slower dehydrogenation rate of 2-propanol over Ni/C. The turnover frequency (TOF) value of Ni/C was comparable to that of Ru/C. Regarding product selectivity, the major products over Ru/C are cyclohexanol (70.2%) and 2-methoxycyclohexanol (11.4%), indicating that hydrogenation of the aromatic ring and demethoxylation readily occur through CTH with Ru/C. Ni/C showed a similar product distribution to Ru/C, producing cyclohexanol (47.7%), 2-methoxycyclohexanol (23.6%), and phenol (15%) as the main products. The formation of phenol over Ni/C indicates that the hydrogenation of the aromatic ring over Ni/C is slower than that over noble metal catalysts, similar to results reported by other groups [3]. Meanwhile, Pd/C showed a significantly different product distribution from Ru/C. Etherified products of 2-propanol and the hydrogenated guaiacol intermediates (e.g., 1-isopropoxy-2-methoxycyclohexane, isopropoxybenzene) are the major products (55.8%) along with a lesser amount of 2-methoxycyclohexanol (18%). This result implies that Pd/C catalyzes the undesired etherification reaction in parallel with the hydrogenation of guaiacol. Overall, the Ru/C catalyst showed the best performance for the CTH of guaiacol, giving the highest yield of cyclohexanol.

In order to produce the fully deoxygenated cyclohexane from guaiacol, a combination of acidic supports and Ru metal was investigated. Alumina (Al_2O_3) and H-Beta zeolite (H-BEA) were selected to probe the reactivity of Lewis and Brønsted acid sites in the reaction, respectively. Ru/Al₂O₃ showed similar guaiacol conversion and product selectivity to Ru/C, indicating that Lewis acids do not promote the

Table 1

Conversion and product selectivity for the CTH of guaiacol in 2-propanol as a solvent at 473 K for 5 h with various catalysts.

Entry	Catalyst	Conv. (%)	Sel. (%)						$TOF(h^{-1})$	IPA Conv. (%)	Sel. (%) from IPA	
			Cyclohexane	Cyclohexanol	2-Methoxy cyclohexanol	Phenol	Others	Ethers			Acetone	Isopropyl ether
1	Ni/C	17.5	1.6	47.7	23.6	14.7	-	-	3471	3.5	81.9	16.8
2	Pd/C	89.3	9.9	1.8	18.3	-	4.8	55.8	2359	5.1	48.5	47.4
3	Ru/C	99.3	0.8	70.2	11.4	-	2.7	4.0	3767	8.0	83.0	16.6
4	Ru/Al_2O_3	99.3	2.2	60.4	12.9	-	4.1	9.0	-	13.0	97.3	2.0
5	Ru/H-BEA	9.9	-	-	-	-	-	77.5	-	42.3	-	94.5

Others are 1,2-cyclohexanediol and cyclohexanone.

Ethers include 1-isopropoxy-2-methoxybenzene, 1-isopropoxy-2-methoxycyclohexane, isopropoxy benzene, and isopropoxycyclohexane.

TOF was calculated based on the guaiacol conversion (at conversion < 20%).

Table 2

CO chemisorption results of Ru/C, Re/C, and Ru-Re/C catalysts with Re/Ru atomic ratios of 0.25, 0.5, and 0.75.

Entry	Catalyst	Ru loading (wt%)	Re loading (wt%)	Re:Ru (mol:mol)	Dispersion (%) ^a	Particle size (nm) ^a
1	RuRe/C	4	1.8	0.25	42.0	3.2
2	RuRe/C	4	3.64	0.5	39.8	3.5
3	RuRe/C	4	5.4	0.75	38.8	3.6
4	Ru/C	4	-	-	55.2	2.4
5	Re/C	-	3.64	-	31.9	4.4

 $^{\rm a}~$ Calculated from CO chemisorption measurements by assuming a stoichiometry of CO/ ${\rm metal}_{\rm atom}=1.$

dehydroxylation of cyclohexanol. Meanwhile, Ru/H-BEA showed a significantly lower conversion of guaiacol (10%), and the major product is 1-isopropoxy-2-methoxybenzene (77%). This result suggests that Brønsted acids inhibit the CTH of guaiacol over Ru by catalyzing the undesired etherification of guaiacol and 2-propanol. Overall, it is difficult to promote the dehydroxylation of guaiacol using an acidic support under CTH conditions. Therefore, we explored the possibility of adding oxophilic promoters to Ru/C to enhance the dehydroxylation activity.

3.2. CTH of guaiacol over RuRe/C catalysts

Bimetallic catalysts that consist of typical hydrogenation metals (e.g., Ru, Rh) with more oxophilic metals (e.g., Re, Mo) have proven to be effective for the hydrogenolysis of C—OH bonds for various biomass-derived molecules. For examples, Tomishige et al. reported that an addition of Re to Rh/SiO₂ markedly enhances the hydrogenolysis activity of glycerol to 1,3-propanediol [20–22]. Dumesic et al. reported that Rh/C catalysts promoted with Re or Mo are highly active for the hydrogenolysis of cyclic ethers (e.g., tetrahydrofurfuryl alcohol) to the corresponding diols [23,24]. Accordingly, we prepared bimetallic RuRe catalysts with different Re:Ru molar ratios for use in the CTH of guaiacol.

3.2.1. Characterization of RuRe/C catalysts

Fig. 1 shows the TPR profiles of the Ru/C, Re/C, and RuRe/C catalysts with Re/Ru atomic ratios of 0.25, 0.5, and 0.75. The TPR curve for each catalyst shows two major peaks: a sharp peak at 393–573 K and a broad peak at 630–1000 K. The broad peak at 630–1000 K is related to the reduction of the surface functional groups of the carbon support, while the sharp peak at 393–573 K is related to the reduction of ruthenium oxide and rhenium oxide. The peak temperatures of the Ru/C and Re/C catalysts appear at 393 K and 573 K, respectively, and the RuRe/C catalysts show a single reduction peak at 433–453 K, which is slightly higher than that of Ru/C but much lower than that of Re/C. It was reported that in the case of bimetallic catalysts containing noble metals such

as Ru and Ir, the noble metals can promote the reduction of the other metal due to hydrogen transfer from their reduced species [25,26]. Therefore, these results suggest that Ru and Re are in close contact on the carbon support, by which hydrogen adsorbed on reduced ruthenium species can easily be transferred to unreduced neighboring rhenium species during the reduction process. In addition, the amounts of H₂ uptake of the catalysts were calculated from the TPR profiles (see Table S1). It was found that the amount of H₂ uptake of the RuRe/C (0.5) was larger compared to the sum of individual amount of H₂ uptake of Ru/C and Re/C. This result indicates that there is a strong interaction between the two metals, changing the reducibility of both metal species.

CO chemisorption measurements were carried out for the reduced Ru/C, Re/C, and RuRe/C catalysts, as shown in Table 2. Ru/C exhibited the highest metal dispersion (55%), while Re/C showed the lowest metal dispersion (32%). For the RuRe/C catalysts, the metal dispersion was in the range of 39–42%, and it decreased with an increase in the amount of added rhenium. TEM analyses were also conducted on the RuRe/C (0.5) catalyst (Fig. S2). The TEM images show highly dispersed metal particles (<2 nm in size) on the carbon support. Overall, the CO chemisorption and TEM results suggest that Ru and Re particles in the RuRe/C catalysts are well-dispersed on the carbon support.

In order to investigate the distribution of Ru and Re on the surface of the carbon support, STEM-EDX analyses were carried out. Fig. 2 shows STEM-EDX mapping images of the reduced Ru-Re/C (0.5) catalyst. These images show that both Ru and Re atoms exist on the surface of the carbon support and that they are evenly distributed on the support. According to the phase diagram for a Ru–Re mixture, the two metals are completely miscible due to their similar atomic sizes and surface energies. Thus, based on the EDX mapping and TPR results, it is believed that Ru–Re bimetallic nanoparticles were formed in the RuRe/C catalysts, resulting in strong interaction between Ru and Re.

3.2.2. Catalytic activity of RuRe/C catalysts

Table 3 shows the catalysis results of the RuRe/C and Re/C catalysts for the CTH of guaiacol at 473 and 513 K in 2-propanol as a solvent. The results show that all of the RuRe/C catalysts are fairly active for the CTH of guaiacol (70–99% conversion) and that they further convert cyclohexanol to cyclohexane. The catalytic activity is a function of the atomic ratio of Re to Ru in the catalysts. The TOF values for the conversion of guaiacol and the cyclohexane selectivity decreased in the order of RuRe/C (0.5) > RuRe/C (0.25) > RuRe/C (0.75). Also, the conversion of 2-propanol showed the similar trend to the conversion of guaiacol, indicating that the rate of 2-propanol dehydrogenation is an important factor determining the activity in the CTH of guaiacol. Compared to the RuRe/C catalysts, Re/C showed significantly lower activity for the CTH of guaiacol (3.2% conversion), presumably due to the slower dehydrogenation rate of 2-propanol over Re/C. However, the major products



Fig. 2. STEM-EDX images of the RuRe/C (0.5) catalyst.

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Conversion and product selectiv	vity for the CTH of guaiacol	in 2-propanol at 473-513 K fo	r 5 h with RuRe/C and Re/C catalysts.
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Entry	Catalyst	Temp	emp Conv. K) (%)	ıv. Sel. (%)						TOF	IPA Conv.	Sel. (%) from IPA	
		(K) (Cyclohexane	Cyclohexanol	2-Methoxy cyclohexanol	Phenol	Others	Ethers	(h ⁻¹)	(%)	Acetone	Isopropyl ether
1	RuRe/C (0.25)	473	94.6	32.3	56.2	3.8	1.6	0.8	3.4	1377	18.0	90.4	8.1
2	RuRe/C (0.5)	473	99.1	38.3	44.7	2.2	-	1.1	4.3	2403	21.9	87.4	8.4
3	RuRe/C (0.75)	473	70.9	30.5	47.5	3.5	12.4	0.8	2.5	798	12.2	92.8	5.2
4	Re/C	473	3.2	9.1	-	-	56.6	-	-	24	2.1	90.2	7.0
5	Ru/C + Re/C	473	37.3	11.3	30.7	1.1	41.3	-	0.6	-	8.9	97.2	1.4
6	RuRe/C (0.25)	513	98.9	46.6	35.1	2.0	-	0.9	5.8	-	26.2	89.0	6.1
7	RuRe/C (0.5)	513	99.0	57.0	24.1	1.1	-	0.7	6.0	-	28.0	83.5	10.7

over Re/C were phenol (56.6%) and cyclohexane (9.1%), suggesting that rhenium is active for the hydrogenolysis of C—OH bonds. Thus, the high activity of RuRe/C catalysts for the production of cyclohexane can be explained by the enhanced hydrogenolysis activity over the Re surface with the Ru-assisted dehydrogenation of 2-propanol. Higher temperatures also promoted the hydrogenolysis of cyclohexanol over RuRe/C catalysts. When the reaction temperature was increased from 473 K to 513 K, the cyclohexane selectivity was increased from 38% to 57% over the RuRe/C (0.5) catalyst at 99% conversion.

The promoting effect of Re species on the hydrogenolysis of Ru/C catalysts can be also explained by its acidic properties. Several researchers suggested that Re promoted Ru/C or Rh/C catalysts have bifunctional active sites composed of metal (for hydrogenation) and acid sites (for dehydration), resulting in a bifunctional pathway for C-O hydrogenolysis involving acid-catalyzed dehydration followed by metal-catalyzed hydrogenation [23,27-29]. They reported that the acidity of the catalysts originated from the presence of rhenium oxide species in the catalysts. Accordingly, XPS analyses of the RuRe/C (0.5) catalysts before and after reaction were carried out to check the presence of rhenium oxide species on the catalyst surface (see Fig. S3). The XPS results showed that the surface rhenium species exist fully as rhenium oxide (ReO₃) in the fresh catalyst and remain as rhenium oxide even after reaction at 473 K, although its oxidation state was slightly changed, forming a mixture of ReO3 and Re2O7. Because the catalyst was exposed to air after the reduction process, it is believed that rhenium oxide was formed in the reduced catalyst. Therefore, the XPS results suggest that rhenium oxide in the RuRe/C catalysts can be the active phase for the CTH of guaiacol.

In order to characterize the presence of surface acid sites on the RuRe/C (0.5) catalyst, NH₃-TPD measurements were also carried out. It was found that the acid site density on the Ru/C catalyst (0.2 mmol/g) was similar to that on the activated carbon (0.2 mmol/g), implying that the acidity of the Ru/C catalyst arises from the support. Meanwhile, the acid site density on the RuRe/C (0.5) catalyst (0.8 mmol/g) was



Fig. 3. Conversion of guaiacol and product yields as a function of reaction time at 473 K with the RuRe/C (0.25) catalyst.

markedly higher compared to Ru/C, indicating that the presence of Re induces the surface acid sites (see Fig. S4). It is also interesting to note that the acid site density on the RuRe/C catalyst was considerably higher than the sum of individual acid site densities of Ru/C and Re/C. It appears that there is a strong interaction (or coordination) between Ru and Re, allowing for the generation of more acid sites than Re alone. Overall, based on these observations, it is believed that the RuRe/C catalyst exhibits bifunctional behavior in the CTH of guaiacol, in which Ru catalyzes the dehydrogenation of 2-propanol and the hydrogenation-hydrogenolysis of guaiacol and ReOx promotes cyclohexane production via hydrogenolysis.

3.3. Reaction evolution

A typical reaction profile of the CTH of guaiacol at 473 K over RuRe/C (0.25) is shown in Fig. 3. The conversion of guaiacol increased monotonically throughout the reaction time, reaching 95% after 5 h. Phenol was identified as the major product during the first hour of the reaction, and it decreased with the reaction time. 2-Methoxycylohexanol and cyclohexanone were also observed, but the yields of both products were low. Cyclohexanol and cyclohexane initially formed at 0.5 h and their yields steadily increased throughout the reaction. The product evolution for the decomposition of 2-propanol during the CTH of guaiacol was also monitored (see Fig. S5). 2-Propanol was readily converted into acetone and H₂ along with a small amount of diisopropyl ether. Based on the above results, the reaction network for the CTH of guaiacol over RuRe/ C is proposed (Fig. 4). Utilizing the hydrogen produced in-situ from 2propanol, guaiacol is initially converted into phenol through demethoxylation and subsequently undergoes hydrogenation to cyclohexanol. Cyclohexane is then produced by the hydrogenolysis of cyclohexanol, which is a slow reaction over RuRe/C.

4. Conclusions

In conclusion, we demonstrated an efficient route for the hydrodeoxygenation of lignin monomer guaiacol via CTH using alcohols as the source of hydrogen and RuRe/C as the catalyst. Ru showed activity superior to those of Ni and Pd for the dehydrogenation of 2-propanol and the hydrodeoxygenation of guaiacol to cyclohexanol (>70% yield). Re promotion of the Ru/C catalysts further enhances the rate of C–O hydrogenolysis, shifting the production distribution to cyclohexane (~60% selectivity). Characterization of the catalysts by TPR, chemisorption, STEM/EDX, and NH₃-TPD suggested that Ru–Re bimetallic nanoparticles were formed with surface acidity. The XPS results revealed that rhenium exists as rhenium oxide on the surface of the RuRe/C catalysts. The enhanced hydrogenolysis activity of the bimetallic RuRe/C catalysts can be attributed to its bifunctional characteristic, by which Ru catalyzes the hydrogenation-hydrogenolysis of guaiacol and ReOx provides acid sites to promote the hydrogenolysis.

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Fig. 4. Reaction network of the CTH of guaiacol to cyclohexane using 2-propanol (isopropyl alcohol (IPA)) as a hydrogen donor and the RuRe/C catalyst. Compounds: 1-isopropoxy-2-methoxybenzene (1), 1-isopropoxy-2-methoxy cyclohexane (2), isopropoxybenzene (3), isopropoxycyclohexane (4).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2016.08.022.

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