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Introduction

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Selective Hydrodeoxygenation of Lignin-Derived Phenols to Alkyl **Cyclohexanols over Ru-Solid Base Bifunctional Catalyst** f f Guang-Yue Xu, Jian-Hua Guo, Yan-Chao Qu, Ying Zhang*, Yao Fu and Qing-Xiang Guo Cyclohexanol and alkyl cyclohexanol are important chemical intermediates. It is meaningful to prepare cyclohexanols from non-fossil-based biomass. Here we report Ru/ZrO₂-La(OH)₃, a metalsolid base bifunctional catalyst, to show its excellent performance on the partial hydrodeoxygenation of lignin-derived phenols. Guaiacol could be converted to cyclohexanol with 91.6% yield in water. Alkyl phenols with one or two methoxy groups were converted into alkyl cyclohexanols with yields over 86.9%. The catalyst had good activity of removing methoxy group and keeping hydroxyl group. In this catalyst, Zr and La interacted with each other to form a mixed (hydr)oxide, thus made ZrO₂-La(OH)₃ a stable support. Ru was highly dispersed on ZrLa support. The pathway from guaiacol to cyclohexanol was investigated and proposed as two parallel ways, Lignin, one of the main constituents of lignocellulosic biomass (15-30% by weight and 40% by energy), is a natural amorphous polymer consisting of methoxylated phenylpropane units.¹⁻⁴ Lignin is also recognized as a potential resource for a wide variety of bulk and fine chemicals, particularly aromatic compounds.^{5,6} Through different methods, such as pyrolysis, hydrogenolysis, biological methods, etc., lignin can be converted into phenolic compounds.⁷⁻¹² These phenolic compounds can be hydrogenated to alkane fuels, aromatic hydrocarbon or used as value-added chemicals.¹³⁻²⁰ Different from fossil-based chemicals, biomass derived chemicals have extensive functional groups. It is obligatory to find effective methods to obtain useful chemicals from biomass through selective catalytic process to tailor the

Cyclohexanol is an important feedstock in industry, which can be converted into cyclohexanone, polymerized to plasticizer, or used as solvent. Alkyl cyclohexanols are also important intermediates in the preparation of spices, medicines, and polymers.^{21,22} Alkyl cyclohexanols can be obtained from the hydrogenation of corresponding alkyl phenols. Nevertheless, the phenolic compounds obtained from lignin always have methoxy groups, such as guaiacol (2-

demethoxylation followed by hydrogenation (I), the saturation of the aromatic ring through hydrogenation and then demethoxylation through direct hydrogenolysis (II). methoxyphenol), eugenol (2-methoxy-4-allylphenol), etc. Simple hydrogenation can not lead to the selective formation of cyclohexanol or alkyl cyclohexanols. Selective removal of methoxy group is necessary in the conversion. Traditional method to produce alkyl cyclohexanols is catalytic hydrogenation of alkyl phenols without methoxy groups. Few studies have been focused on the selective conversion of lignin derived methoxyphenols to alkylcyclohexanols. Wang et al. converted phenol compounds and bio-oil derived phenolic compounds to cyclohexanols and less functionalized alkyl phenols with Raney Ni and isopropanol (hydrogen donor).²³ Nakagawa et al. applied Ru/C combined MgO to convert guaiacol to cyclohexanol and methanol with 80% yield at 160 °C and 1.5 MPa H₂.²⁴ The presence of base promotes the demethoxylation step and suppresses the unselective C-O dissociation. However, MgO is not stable in aqueous solution. Recently, Long et al. used Ni/MgO to produce cyclohexanol from guaiacol in decahydronaphalene with 97.74% yield at 160 $^\circ C$ and 3 MPa H_2 . 25 Ni/CeO_2 was employed by Sels et al. to convert alkylmethoxylphenols into alkylcyclohexanols at 250-300 °C.²⁶ Ru-Mn catalyst was used by Tomishige et al. to selectively cut the methoxyl group on substituted phenols to produce cyclohexanol with 81% yield at 160 °C and 1.5 MPa H₂. Although there is some promising progress, the development of new efficient catalytic systems is still necessary to convert methoxyphenols to cyclohexanols with high selectivity and stability.

> In our previous work, we found that 5 wt% Ru/SBA-15 catalysts had a good activity to convert phenols separated from bio-oils into C_6 - C_{10} alcohols at 170 °C in isopropanol.²⁸ Besides, ZrO₂-La₂O₃ was reported as a good solid base with high stability.²⁹ Based on the fact that Ru catalysts always

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display good performance in phenolic compounds hydrogenation and the promotion effect of base in the conversion of methoxy phenols, we develop a new catalytic system to selectively transform methoxyl phenols to cyclohexanol and alkyl cyclohexanols over bifunctional catalysts in water.

Experimental

La(NO₃)₃ ·6H₂O (99.99% metals basis), RuCl₃·xH₂O (Ru% \geq 37.5 %) were purchased from Aladdin Reagents (Shanghai) Co., LTD. Zr(NO₃)₄·5H₂O (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. ZrO₂ was obtained from Saint-Gobain Norpro. All chemicals were obtained commercially and used without further treatment.

Preparation of the catalysts

 ZrO_2 was obtained from Saint-Gobain Norpro. Since La_2O_3 is easy to be converted to corresponding hydroxides in water, the catalysts were directly prepared as Ru/hydroxide. The $La(OH)_3$ and ZrO_2 - $La(OH)_3$ with different Zr:La molar ratios (4, 2, 1) were prepared by precipitation method. First, certain amounts of $La(NO_3)_3$ · GH_2O and $Zr(NO_3)_4$ · SH_2O were dissolved in 200 mL of water and stirred for 2 h. Then 2 M ammonia hydroxide was added into the mixture to adjust the solution pH to 10 and stirred at room temperature for another 2 h. Then the solid was filtrated, washed and dried over night at 105 °C. After calcined at 700 °C for 4 h, the solid was stirred for 2 h in water. The La(OH)_3 and ZrO_2 -La(OH)_3 with different Zr:La ratios were obtained after filtrated and dried at 40 °C for 12 h.

The 5 wt % Ru/ZrO₂, 5 wt % Ru/La(OH)₃, and 5 wt % Ru/ZrO₂-La(OH)₃ with different Zr:La ratio (4, 2, 1) were prepared by deposition-precipitation method. RuCl₃·3H₂O was dissolved in water, and a calculated amount of carrier was added to this solution and stirred at room temperature for 2 h. Then ammonia hydroxide was added into the mixture to adjust the solution pH to 10 and stirred at room temperature for another 2 h. After filtering, washing and drying over night at 40 °C, the catalysts were reduced in a H₂ and N₂ atmosphere at 280 °C for 3 h. The flow rate of hydrogen and nitrogen was 10 and 100 mL/min, respectively. The catalysts prepared above were labelled as RuZr, RuZrLa-4 RuZrLa-2, RuZrLa-1, and RuLa.

Catalysts Characterization

Nitrogen adsorption measurements were performed using a Coulter SA 3100 adsorption analyzer which reports adsorption isotherm, specific surface area and pore volume automatically. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area in the range of relative pressures between 0.05 and 0.20. The pore sizes were calculated from the adsorption branch of the isotherms using the thermodynamic based Barrett-Joyner-Halenda (BJH) method.

The metal content in catalysts and liquid residue were analyzed by an Optima 7300 DV ICP-OES.

XRD analysis was conducted on an X-ray diffractometer (TTR-III, Rigaku Corp., Japan) using Cu K α radiation (λ = 1.54056 Å). The data were recorded over 2 θ ranges of 10-70°.

The pH value of the catalyst-water mixtures was measured by Mettler Toledo 320-S pH Electrodes. The catalyst-water mixtures were prepared as follow: 0.10 g catalyst was added in 20 mL H_2O and stirred for 30 min.

XPS analysis was conducted on an X-ray photoelectron spectrometer (ESCALAB250, Thermo-VG Scientific, USA) at room temperature under a vacuum of 10^{-8} - 10^{-9} torr using monochromatized Al K α radiation (1486.92 eV).

 $\rm H_2\text{-}TPD$ analysis was carried out on a self-built chemical adsorption instrument. 80 mg of catalyst was loaded in a quartz tube and was reduced at preparation condition. After cooling down to room temperature, the adsorption process was conducted in a 5% H₂/Ar flow (60 mL/min) for 1 h followed by sweeping in Ar flow (40 mL/min) for 1 h to remove physical adsorbed species. During the desorption process, the sample cell was heated up at a ramping rate of 10 °C/min to 450 °C in Ar flow (40 mL/min), and the TPD data was recorded. An icesalt trap with KOH filling was used to remove water and CO₂ (absorbed on La species when the catalyst was exposed to air) formed during the tests.

HAADF-STEM images and EDS mapping analysis were taken with a JEOL-2100F field emission transmission electron microscopy.

DSC-TGA was taken by an SDT Q600 V20.9 Build 20 in air atmosphere.

Experimental Procedure

Typical procedure for hydrogenation of phenolic compounds: guaiacol (5 mmol) and 5% Ru–based catalyst (0.10 g), solvent (20 mL H₂O) were mixed in a Parr reactor (316L stainless steel, 50 mL reactor volume with a quartz lining). After purging the reactor with H₂, the autoclave was pressurized with 4 MPa H₂ at room temperature and then heated at 170 °C for 4 h at a stirring speed of 1000 rpm. The heating rate was 10 °C/min. After the reaction was halted, the reactor was put into cold water until cooled down to room temperature. The liquid product was extracted by ethyl acetate, and the aqueous phase was also collected. The aqueous and organic layers were both analyzed by GC (Kexiao 1690) and GC-MS (Agilent 7890A). *n*-Hexanol was used as the internal standard to determine the product amount.

The conversion and yield were calculated by mol%.

Conv.(%)=(1 molaramount of guaiacolafter reaction
	molaramount of guaiacolin the starting material
$\operatorname{Yield}(\%) = -$	molar amount of each product
	molar amount of guaiacol in the starting materia

The separated catalyst was dried at 40 °C after filtration and acetone sequential washing. During the catalyst stability test, the catalyst was reused without any further treatment.

Results and discussion

Catalyst Characterization

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Table 1. Characteristics of the Ru-based catalysts.

Code	Ru (wt%)	S _{BET} (m ² g ⁻¹)	V_{pore} (cm ³ g ⁻¹)	d _{pore} (nm)
RuZr	4.85	58.3	0.26	15.3
RuZrLa-4	4.92	43.6	0.20	14.2
RuZrLa-2	4.90	40.4	0.22	14.6
RuZrLa-1	4.93	38.4	0.17	14.5
RuLa	4.99	17.7	0.07	12.3

In this work, a series of Ru-based catalysts were prepared. The main characteristics of the Ru-catalysts are shown in Table 1. The Ru/ZrO₂, Ru/La(OH)₃, and Ru/ZrO₂-La(OH)₃ with different Zr:La ratio were labelled as RuZr, RuLa, RuZrLa-X (X=4, 2, and 1). The RuZr catalyst had the highest surface area (58.3 m² g⁻¹), the largest pore volume (0.26 cm³ g⁻¹), and the largest pore diameter (15.3 nm). The surface area of the catalysts decreased with the rise of La content. The pore volume and the average pore diameter were similar among the RuZrLa catalysts, while they are lowest with RuLa catalyst.

Figure 1 shows the powder XRD patterns of Ru-catalysts with different supports. No peaks of Ru were observed in the XRD patterns, which indicated that Ru existed in an amorphous state or well dispersed in catalysts. The peaks in the RuZr catalyst corresponded to the diffraction peaks of ZrO_2 (JCPDS Card No. 37-1484). The peak intensity of ZrO_2 planes decreased with the decrease of Zr content. The peaks in RuLa catalyst corresponded to the diffraction peaks of La(OH)₃ (JCPDS Card No. 36-1481) and La₂O₂CO₃ (JCPDS Card No. 37-0804). In RuZrLa-1 and RuZrLa-2 catalysts, the peaks of La(OH)₃ could be observed obviously. As more Zr adding, the RuZrLa-4 revealed mainly ZrO₂ with weak diffraction peaks of La(OH)₃.

Catalysis

As a model compound, guaiacol was chosen to investigate the effect of the catalysts on converting methoxyphenols into the corresponding alcohols. Table 2 shows the hydrogenation of guaiacol in water with Ru catalysts supported on different carriers. The main products were cyclohexanol, 2methoxycyclohexanol and cyclohexane (Scheme 1). Trace other intermediates were also detected, such as methoxycyclohexane and 1,2-cyclohexanediol. Methane and methanol were both detected C1 products. When the reaction was conducted for 4 h at 170 °C, 4 MPa H₂ in the presence of RuZr (Table 2, entry 1), the primary products were cyclohexanol (58.1%), 2-methoxycyclohexanol (36.2%), and cyclohexane (4.3%). Previous study indicated that the presence of base can promote the demethoxylation step and suppress the unselective C-O dissociation. ²⁴ When the reaction took place in 0.5 wt% KOH solution instead of pure water with Ru/ZrO₂ as catalyst (Table 2, entry 2), the yield of cyclohexanol increased from 58.1% to 81.8%, while the yield of 2methoxycyclohexanol decreased from 36.2% to 15.5% simultaneously. KOH without Ru catalysts revealed no catalytic activity (Table 2, entry 3). Usually, it requires extra effort to





Figure 1. XRD patterns of the Ru catalysts.

recycle alkaline solution for the environmental and economic concerns, so Ru-solid base bifunctional catalyst should be a good choice for the selective hydrodeoxygenation of methoxyphenols. Ru/MgO (RuMg) catalyst was prepared for MgO is a typical solid base. The mixture of RuMg and water showed alkaline (Table S1, entry 2). 66.8% cyclohexanol was obtained by using RuMg as catalyst (Table 2, entry 4). However, RuMg was not stable in hot water since it became muddy after reaction because of the hydration of MgO. The yield of cyclohexanol was barely satisfactory, which might be attributed to the instability of RuMg. The mixture of RuLa and water was alkalescent (Table S1, entry 3)and 75.2% cyclohexanol was obtained by using RuLa as catalyst (Table 2, entry 5). The solid base ZrO₂-La(OH)₃ could be an appropriate carrier of Ru-based catalyst. According to the data of Table S1, the mixtures of RuZrLa catalysts with different Zr/La ratios and water were alkaline and had higher pH value than that of RuLa and RuZr. The yield of cyclohexanol was 81.6% when RuZrLa-2 was used as catalyst. When the reaction time doubled to 8 h, the yield increased slightly to 85.1%. Temperature is a significant factor in the reaction. As the temperature increased to 200 °C, the guaiacol could be converted into cyclohexanol with an excellent yield of 91.6%. Higher temperature was appropriate for the demethoxylation reaction. While the temperature was further increased to 230 °C, cyclohexanol further converted to cyclohexane with a certain yield of methane as well as ethane and propane via the C-C bond cleavage over Ru. Comparing the structures of guaiacol and cyclohexanol, RuZrLa-2 catalyst had a good activity of removing methoxy group and keeping hydroxyl group under relative mild conditions. Then the catalyst was reused for another run at 170 °C. The yield of cyclohexanol decreased from 81.6% to 73.3%. While, the yield of cyclohexanol decreased from 75.2% to 58.1% by using RuLa. Therefore, RuZrLa-2 catalyst was more stable than pure RuLa catalyst. The

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Scheme 1. The hydrogenation of guaiacol.

Table 2. The effect of catalysts in the hydrogenation of guaiacol. ^a

- ·				Yield/%				
Entr	Entr Catalyst		Conv	-	6		Meth	Meth
У		C	./ %	а	D	С	-anol	-ane
1	RuZr	170	99.1	36.2	58.1	4.3	24	33
2 ^{<i>b</i>}	RuZr+KOH	170	99.4	15.5	81.8	0.2	22	50
3 ^b	КОН	170	0	0	0	0	0	0
4	RuMg	170	100	32.7	66.8	0.3	17	44
5	RuLa	170	100	23.8	75.2	0.5	19	40
6	RuZrLa-4	170	100	19.4	77.3	1.1	14	55
7	RuZrLa-2	170	100	15.4	81.6	0.2	17	61
8	RuZrLa-1	170	100	17.7	78.6	0.2	15	56
9 ^{<i>b</i>}	RuZrLa-2	170	100	6.6	89.9	0.1	15	69
	+KOH							
10 ^c	RuZrLa-2	170	100	11.1	85.1	0.5	11	63
11	RuZrLa-2	200	100	5.8	91.6	1.3	4	93
12	RuZrLa-2	230	100	0	2.2	42.8	2	350
13 ^d	RuZrLa-2	170	100	20.2	73.3	2.3	13	56
14 ^{<i>d</i>}	RuLa	170	100	31.7	58.1	0.7	15	39

^{*a*} Reaction conditions: 5 mmol guaiacol, 0.10 g 5 wt% Ru-based catalyst, 20 ml H_2O , 4 MPa H_2 , 4 h, reaction mixture stirred at 1000 rpm. ^{*b*} Solvent: 20 mL 0.5 wt% KOH solution. ^{*c*} Reaction time 8h. ^{*d*} The catalyst used for the second run.

metal losses based on the original catalyst in the liquid residue were shown in Table S2. In RuLa catalyst, the La loss (0.903 wt%) was much higher than that in RuZrLa catalysts (between 0.061 to 0.125%). The losses of Ru (between 0.041 to 0.052 wt%) and Zr (between 0.007 to 0.018 wt%) were similar (Table S2). It indicated that the ZrO_2 -La(OH)_3 supports were more stable than pure La(OH)_3 support. As the amount of leached metals on RuZrLa-2 catalyst was quite small, the activity loss may caused by coke deposition on the catalyst. Both fresh and used catalyst were characterized by TGA under air atmosphere. From TGA curves shown in Figure S1, the remarkable weight loss of the used catalyst at about 336 °C proved the existence of coke.

Apart from guaiacol, the RuZrLa-2 was also tested in the hydrodeoxygenation of more complex methoxyphenols, which with more alkyl or methoxy groups, in water at 200 °C. A similar selectivity for alkyl cyclohexanols (88.7-89.5%) was obtained with the phenols which had one methoxy group, including 2-methoxy-4-ethylphenol, 2-methoxy-4-propyl-phenol, and 2-methoxy-4-allylphenol. However, the selectivity for alkyl cyclohexanols decreased when 2,6-dimethoxyphenol and 2,6-dimethoxy-4-allylphenol were used as substrates. It indicated that extra methoxy group on the benzene ring would increase the difficulty of demethoxylation reaction. When the reaction time was extended to 8 h, a higher yield could also be achieved.

Table 3. Hydrodeoxygenation of lignin-derived methoxyphenols.^a



 $[^]a$ Reaction conditions: 5 mmol reactant, 0.10 g RuZrLa-2, 20 ml H₂O, 4 MPa H₂, 200 °C, 3 h, reaction mixture stirred at 1000 rpm. b Reaction time: 8 h.

Discussion

why RuZrLa catalysts showed To explain better performance on selectively converting methoxyphenols to allylphenol, a series of characterazation and analyses were carried out. The XPS spectra showed the chemical properties of Ru catalysts, as shown in Figure 2. The straight dotted lines showed the binding energy of each species in RuZrLa-2 catalyst. The Zr and La species were not simple mixed, but interacting with each other. In the ZrLa support, Zr donated electron to La to make a relative electronegative Zr and electropositive La, like $Zr^{4-\delta}O_2-La^{3+\delta}(OH)_3$ mixed (hydr)oxide species. As Zr content increasing, the binding energy of Zr 3d shifted to high value while that of La 3d shifted oppositely to low value. This tight interaction effect made ZrO₂-La(OH)₃ a stable material, which could explain the much lower La loss in RuZrLa catalysts. The chemical shifts of Ru 3p were also in keeping with the experimental results. The binding energies of Ru 3p on RuZrLa catalysts were higher than that on RuLa or RuZr catalysts. As is known, the binding energy of nanoclusters increased with the size decreasing.³⁰ A smaller metal particle size would lead to higher surface area of metal and thus gave rise to better catalytic activity. In RuZrLa-2 catalyst, the binding energy of Ru 3p was the highest among the catalysts, which could lead to the prominent catalyst activity of RuZrLa-2 catalyst. To compare the Ru dispersion of the catalysts, H₂-TPD was carried out, as shown in Table S3 and Figure S2. RuZrLa-2 showed the highest H_2 uptaken amount among the catalysts, and it matched well with the variation tendency of binding energy and catalytic activity.

According to the electronic image by HADDF-STEM, as shown in Figure 3, the RuZrLa-2 catalyst was random spontaneous stacked clusters. EDS mapping results were

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Figure 2. XPS spectra of (top) Zr 3d, (middle) La 3d and (bottom) Ru 3p in Ru catalysts. The binding energies were calibrated to the carbon with C 1s band.

employed to show the distribution of each element. There was little distinction between Zr and La distribution, which further proved the interaction between ZrO_2 and $La(OH)_3$. Considering of the XPS results, the ZrLa support was a mixed (hydr)oxide rather than isolated or simple mixed ZrO_2 and $La(OH)_3$ species. Because of the similar contrast with La, the Ru nanoparticles could hardly be directly observed in STEM image. However, it can be observed that Ru was highly dispersed on ZrLa support from the EDS result.

Reaction Pathways

To further investigate the process of the selective hydrodeoxygenation of lignin-derived methoxyphenols,



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Figure 3. EDS mapping of RuZrLa-2 catalyst.



Figure 4. Product distribution after the hydrogenation of guaiacol at 200 °C with RuZrLa-2. It took 15 min to heat up to 200 °C. Time -0.25 h is the start of heating up while time 0 h means temperature reaches 200 °C.

guaiacol was hydrotreated at 200 °C over RuZrLa-2. The change of the main products distribution with time is shown in Figure 4. The conversion of guaiacol reached 94% at the beiginning of the reaction, and no unsaturated products were detected after 0.5 hours. The primary products were cyclohexanol (42%) and 2-methoxycyclohexanol (50%) at 0 h (The reaction was terminated immediately once the temperature reaches 200 °C by cold water). The yield of cyclohexanol increased with the extension of reaction time and reached the highest yield (91.6%) at 4 h, while the yield of 2-methoxycyclohexanol decreased in the same time period. Only small amount of cyclohexane (<2.5%) was formed via the hydrodeoxygenation during the conversion. Trace methoxycyclohexane (< 0.1%) and 1,2-cyclohexanediol (< 0.1%) were also detected by the GC-MS.

To further study the reaction pathway, the main intermediates detected in guaiacol hydrogenation were used as reactants (Table 4). Methoxycyclohexanol was the most important intermediate detected in the guaiacol conversion

hydrogenation.

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process. The conversion of 2-methoxycyclohexanol was 87% and the main product was cyclohexanol under the same operating conditions. Three ways could exist to achieve cyclohexanol from methoxycyclohexanol: directly demethoxylation to cyclohexanol, hydrogenolysis of methoxy group to 1,2-cyclohexanediol, and dehydroxylation of hydroxy group to methoxycyclohexane.²⁴⁻²⁶ Both 1,2-cyclohexanediol and methoxycyclohexane were employed as feedstock under the same operating conditions. The conversion of 1,2cyclohexanediol was 63% and the main product was cyclohexanol. Suppose that hydrogenolysis of methoxy group to 1,2-cyclohexanediol was a main route, there should be a certain amount of 1,2-cyclohexanediol detected due to the relatively slow reaction rate of 1,2-cyclohexanediol. However, only trace 1,2-cyclohexanediol was detected in the reaction. It revealed that the hydrogenolysis was not a main route. Likewise, the methoxycyclohexane showed a lower conversion with 35% cyclohexane selectivity while only trace amount of methoxycyclohexane was detected as intermediate, so the dehydroxylation was not a main route, either. Meanwhile, when cyclohexanol was employed as feedstock, it was hard to transform to cyclohexane. The selectivity of cyclohexane was low from guaiacol but high from methoxycyclohexane, which further denied the dehydroxylation route. Considering that the hydrogenation process was very quick under this condition, the reaction was terminated during increasing temperature to catch the intermediate products. The reactor was put into cold water just when the temperature reached 150 °C. The conversion of guaiacol was 67%, and the selectivity of cyclohexanol and 2-methoxycyclohexanol were 47.2% and 49.8%, respectively. Trace phenol (1.2%) and anisole (0.2%), which came from the demethoxylation and dehydroxylation of guaiacol, could be detected in GC-MS. Experiments with less catalyst (0.01 g) lead to similar result (0.1% phenol was detected). When anisole was tested under same operating conditions, the selectivity of cyclohexane was 32%. If the majority of guaiacol was converted to anisole, more cyclohexane could be found in the products. Comparing with the product distribution of guaiacol, this is not the main route. Phenol can be hydrogenated to cyclohexanol with high conversion and selectivity. According to the conversion of 2methoxycyclohexanol was 8%, and the yield of cyclohexanol was 42%, the cyclohexanol could come from the demethoxylation of guaiacol followed by hydrogenation to cyclohexanol. Phenol was not detected at 200 °C could be due to its high reaction speed. Furthermore, as shown in Table 2, methanol was detected after reaction as the side product of demethoxylation. While methane was also detected, which could be produced by the hydrogenolysis of methanol. Comparing entries 7, and 10 in Table 2, the ratio of methane to methanol increased with reaction time extending. Since during the extending time, the main reaction pathway could not change, methane should come from methanol. Further comparing entries 7, 11 and 12 in Table 2, the ratio of methane increased with temperature increasing, which was because that high temperature was in favor of methanol hydrogenolysis.



Table 4. Hydrogenation of main products detected in guaiacol







Accordingly, the main pathway for the conversion of guaiacol is given in Scheme 2. There are two main routes in the hydrogenation of guaiacol. Guaiacol was converted to phenol via demethoxylation process, and then converted to cyclohexanol via hydrogenation (I). Guaiacol was converted to 2-methoxycyclohexanol through the saturation of aromatic ring followed by the demethoxylation to cyclohexanol (II). Therefore this catalyst was benefit for the demethoxylation reaction.

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Conclusions

In conclusion, a bifunctional RuZrLa catalyst was used in the selective hydrodeoxygenation of lignin-derived phenolic compounds to cyclohexanol and alkyl cyclohexanols, which can be used as chemical feedstock. Over 88% yield of cyclohexanols can be obtained from monomethoxysubstituted phenols hydrotreated at 200 °C for 4 h. The extra methoxy group would decrease the selectivity for cyclohexanols. Longer reaction time can increase the selectivity and yield effectively. In RuZrLa catalyst, Zr and La interacted with each other to form a mixed (hydr)oxide, thus made ZrLa a stable material. Ru was highly dispersed on ZrLa support. RuZrLa-2, with a Zr/La ratio of 2, showed the highest activity in the reaction. The main pathway to form the cyclohexanols from lignin-derived phenolic compounds including two ways simultaneously.

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