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Hydrotreating of Phenolic Compounds Separated from Bio-oil to Alcohols

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Supporting Information

ABSTRACT: Phenolic compounds in bio-oil are not stable and difficult to be upgraded to ideal fuels. In this study, simulated bio-oil as well as phenolic compounds separated from bio-oil by glycerol-assisted distillation were hydrotreated by Ru/SBA-15 catalyst and completely converted into C₃ to C₁₀ alcohols at mild conditions, which could be a feasible way to transfer the phenolic compounds in bio-oil or other real systems from lignin decomposition into high heating-value liquid fuel or fuel additives. The stability of the Ru/SBA-15 catalyst was also investigated. It was found that Ru/SBA-15 was stable with phenolic compounds in the simulated bio-oil but not in a real one.

1. INTRODUCTION

Fast pyrolysis technology can convert biomass into liquid product (known as bio-oil) effectively, which is recognized as one of the most potential methods for resolving the current energy crisis.^{1–3} However, the composition of bio-oil is rather complicated, which leads to corrosiveness and instability of bio-oil.^{4,5} A great amount of effort has been focused on bio-oil upgrading. However, most of those processes are hardly efficient and finally result in catalyst deactivation and reactor clogging owing to the thermal instability of bio-oil.^{6–9} Since direct upgrading of bio-oil is very difficult, separation of bio-oil and upgrading the fractions respectively is a reasonable way.

Bio-oil consists of hundreds of organic compounds, mainly including acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, and a large proportion of lignin-derived oligomers. Applicable technology can make those compounds promising fuel alternatives. Since many compounds in the bio-oil have poor thermal stability, the bio-oil cannot be separated by a conventional distillation process. The introduction of glycerol, a kind of high boiling solvent, can help to stabilize the bio-oil in the distillation process.¹⁰ With glycerol-assisted distillation technology, bio-oil can be separated into distillate and pyrolytic lignin. The pyrolytic lignin in the bio-oil is involatile and thermally instable. It increases the difficulty of bio-oil upgrading. The separated pyrolytic lignin can be converted to alkanes as fuel additives or phenol compounds as a substitute to produce resin.¹¹ The low-molecular-weight compounds in the distillate, such as acetic acid, aldehyde, etc., are able to be purified to produce value-added chemicals via a conventional method. However, phenolic compounds in the real system are instable and always difficult to be handled.^{6–9,12} Hydrogenation is an efficient method to deal with phenolic compounds. Recently, Kou and co-workers reported a series of outstanding works which employed metal–acidic bifunctional catalysts in water system to convert phenolic compounds into alkanes.^{13,14} 300 °C was required for the conversion of eugenol. However, this temperature is limited for bio-oil upgrading due to its thermal instability. Considering that oxygen-containing compounds have better combustion proper-

ties and the conversion requires milder conditions, herein, we used a modified glycerol-assisted distillation technology to separate phenolic compounds from bio-oil and developed an efficient method for hydrotreating either pure phenolic compounds or the ones separated from bio-oil to alcohols. The catalysts were characterized by N₂ adsorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high frequency infrared absorption carbon–sulfur analysis, thermogravimetric analysis (TGA), and differential thermal analysis (DTA).

2. EXPERIMENTAL SECTION

2.1. Materials. RuCl₃·xH₂O (Ru% ≥ 37.5%), PdCl₂ (Pd% ≥ 60%), Pd/C (5 wt %), Ru/C (5 wt %), and eugenol (99%) were purchased from Shanghai Aladdin Reagent Co., Ltd. Triblock copolymer EO₂₀PO₇₀EO₂₀ (P₁₂₃) was purchased from Aldrich. Guaiacol (≥99.0%, CP), phenol (≥99.5%, AR), acetic acid (≥99.5%, AR), furfural (>99.0%, AR), anisole (CP), formic acid (98%, AR), CH₂Cl₂ (≥99.5%, AR), ethanol (≥99.7%, AR), *n*-propanol (≥99.0%, AR), *n*-butanol (≥99.5%, AR), and isopropanol (≥99.7%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

The simulated bio-oil was the mixture of 15 wt % of eugenol, 15 wt % of guaiacol, 15 wt % of phenol, 15 wt % of furfural, 15 wt % of acetic acid, and 25 wt % of water. The bio-oil was obtained from our laboratory through flash pyrolysis of rice husk at about 550–600 °C.¹⁵

The phenolic compounds separated from bio-oil were obtained by a modified glycerol-assisted distillation technology according to the ref 15 as follows: 50 g of glycerin was added into 500 g of bio-oil, and then the mixture was distilled with mechanical stirring. The first distillate (about 300 g) was collected under 120 °C, and then, the second distillate, mainly

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consisting of phenol derivatives used as the starting materials in this study, was collected at 120 °C under vacuum condition (0.1 atm), and about 50 g was obtained. The residue was the mixture of pyrolytic lignin and glycerin (about 184 g).

2.2. Catalyst Preparation. SBA-15 was self-prepared according to the refs 16 and 17. The 5 wt % Ru/SBA-15 was synthesized by strong electrostatic adsorption (SEA) technology according to reference 18: 0.40 g of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was dissolved in 20 mL of deionized water, followed by addition of ammonia to increase the pH value to 11. SBA-15 (3 g) was dispersed in 150 mL of deionized water, and the pH value was also adjusted to 11 by adding dilute ammonia. After stirring for 1 h, Ru(III) solution was added into SBA-15 suspension with stirring for 15 min, and then, the solid was then filtered, rinsed with deionized water to a neutral pH, and dried overnight at 40 °C. The resulting solid was reduced in hydrogen and nitrogen atmosphere at 280 °C for 3 h at a heating rate of 1.0 °C/min to obtain the ultimate catalyst Ru/SBA-15. The flow rate of hydrogen and nitrogen was 10 and 100 mL/min, respectively. The 5 wt % Pd/SBA-15 was synthesized according to the same process.

2.3. Characterization of Catalysts. XRD analysis was conducted on a Philips X'Pert PROS X-ray diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The data were recorded over 2θ ranges of 0.8–5° and 10–70°. The crystal size of the metal was calculated by Scherrer formula.

Nitrogen adsorption measurements were performed using a Coulter SA 3100 adsorption analyzer which reports adsorption isotherm and 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 size distributions were calculated from the adsorption and desorption branches of the isotherms using the thermodynamic based Barrett–Joyner–Halenda (BJH) method. The total pore volume was determined from the adsorption and desorption branches of the nitrogen isotherms at $P/P_0 = 0.98$.

XPS was obtained with an X-ray photoelectron spectroscopy (ESCALAB250, Thermo-VG Scientific, USA) using monochromatized Al K α radiation (1486.92 eV). Ru 3p signals were collected and analyzed by deconvolution of the spectra using XPS Peak 4.1 software, mixed Gauss–Lorentzian (G:L = 70:30) function, and Shirley background.

TGA and DTA of the catalysts were carried out over the range of 25–800 °C at a rate of 10.0 °C/min under air using a DT-60H Thermogravimetric Analyzer, and the gas flow rate was 50 mL/min. The catalysts were dried in air at 200 °C for 3 h before the tests of TGA-DTA. The carbon content of the catalysts was determined by a high frequency infrared carbon–sulfur analyzer (CS-600 series, LECO, USA).

2.4. Experimental Procedure. In a typical test, a certain amount of starting material (eugenol, simulated bio-oil, or phenolic compounds separated from bio-oil) and 5 wt % Ru/SBA-15 were added to a Parr reactor (reactor volume, 50 mL). After purging the reactor with H_2 , the reaction was carried out with 4 MPa H_2 (room temperature) at a series of temperature for 4 h with a stirring speed of 1000 rpm. Subsequently, the reactor was cooled to room temperature. The gas, liquid product, and solid were taken out for further analysis. The catalyst was dried at room temperature after filtration and ethanol sequential washing. During the catalyst stability test, the catalyst was then reused without any further treatments.

2.5. Characterization of Products. The liquid product was analyzed by gas chromatography (GC) and GC-mass spectroscopy (GC-MS). GC and GC-MS analyses were performed on a Kexiao 1690 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m \times 0.25 mm \times 0.25 μm fused-silica capillary column (OV1701, China), and a GC (Agilent 7890A)–mass spectrometer detector (Agilent 5975C with Triple-Axis Detector) (GC–MSD) with a DB-5 capillary column (30 m \times 0.32 mm \times 0.25 μm , Agilent Technology). Anisole was chosen as the internal standard to determine the conversion rate of eugenol: conversion = (1 – amount of eugenol after hydrogenation/total amount of eugenol in the starting material) \times 100%. The gas was analyzed by GC with a thermal conductivity detector (TCD). The gas component was analyzed by GC (GC1609, Kexiao, China) with a TCD using an external standard method. The calibration gas mixture (including H_2 , CO, CO_2 , CH_4 , C_2H_6 , and C_3H_8) obtained from WeiChuang Specialty Gas (Shanghai) was used to determine the distribution of the gas products.

3. RESULTS AND DISCUSSION

3.1. Study of Model Compound. Phenolic compounds in bio-oil mainly consisted of phenol, guaiacol, eugenol, and their derivatives. Eugenol was selected as the model compound to investigate the hydrogenation conditions.^{19–21} Initially, the effect of different solvents on hydrogenation was studied using Ru/SBA-15 as catalyst. Referring to Han and co-workers' research, CH_2Cl_2 was chosen as the solvent.²² The reaction was carried out at 120 °C in a 50 mL Parr autoclave made of 316 stainless steel, but no eugenol conversion was detected by the following GC analysis. Because hydrogen chloride could be produced from the thermal decomposition of CH_2Cl_2 at higher temperature, some thermostable solvents were chosen and tested. From Table 1, it could be seen that, among those

Table 1. Effect of Solvents for Hydrotreating^a

entry	$T/^\circ\text{C}$	solvent	conv./% ^b
1	120	CH_2Cl_2	0
2	170	ethanol	12.24
3	170	<i>n</i> -propanol	52.67
4	170	<i>n</i> -butanol	50.67
5	170	isopropanol	100
6 ^c	170	isopropanol	3.17

^aReaction conditions: eugenol (1.00 g, 6.03 mmol), 5 wt % Ru/SBA-15 (0.20 g, 9.90×10^{-2} mmol Ru), solvent (25 mL), 4 MPa H_2 , and reaction mixture stirred at 1000 rpm for 8 h. ^bThe conversion of eugenol was measured by gas chromatography (GC1690, Kexiao, China) using anisole as an internal standard. ^c4 MPa N_2 was used instead of 4 MPa H_2 .

solvents, isopropanol (*i*-PrOH) was the most proper candidate for hydrotreating, and the results agreed well with reference 23. To test the effect of *i*-PrOH, N_2 was used instead of H_2 at the same condition. Only a minute amount of alcohols were obtained after reaction; the conversion was just 3.17% (Table 1, entry 6). This may indicate that *i*-PrOH does not act as a hydrogen donor in this reaction. The mechanism for action of *i*-PrOH is obscure at present and needs further study.

From Figure 1, it can be seen that a benzene ring of eugenol was completely reduced and cyclohexanol derivatives were produced. A small amount of propylcyclohexane and 4-propylcyclohexanone were also detected. All these reduced

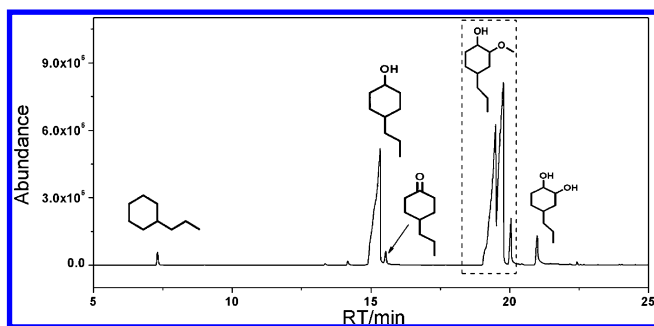


Figure 1. GC-MS spectrum after hydrogenation of eugenol. Reaction conditions: eugenol (1.00 g 6.03 mmol), 5 wt % Ru/SBA-15 (0.10 g 4.95×10^{-2} mmol Ru), *i*-PrOH (25 mL), 4 MPa H_2 , 120 °C, and reaction mixture stirred at 1000 rpm for 4 h.

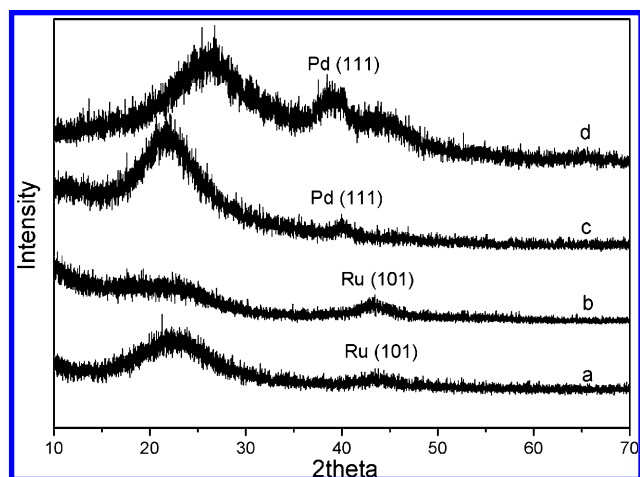


Figure 2. XRD patterns of catalysts: (a) Ru/SBA-15, (b) Ru/C, (c) Pd/SBA-15, and (d) Pd/C.

products derived from bio-oil were high heating-value liquids with good combustion properties.

During the experiments, the influence of different catalysts, such as Ru/SBA-15, Ru/C, Pd/SBA-15, and Pd/C on eugenol hydrogenation was also investigated. The XRD patterns of all the catalysts are shown in Figure 2. The diffraction peaks at $2\theta = 44^\circ$ and 40.1° were indexed to Ru (101) and Pd (111), respectively. According to the Scherrer formula, the crystallite size of noble-metal on Ru/SBA-15, Ru/C, Pd/SBA-15, and Pd/C were about 2.2 nm, 2.7 nm, 3.2 nm, and 3.5 nm, respectively. As shown in Table 2, ruthenium was more active in the hydrotreating reaction compared with palladium, which was in accordance with ref 24. The performance of self-prepared Ru/

Table 2. Effect of Catalyst for Hydrotreating^a

entry	catalyst	catalyst/g	T/°C	P_{H_2} /MPa	t/h	conv./%
1	Pd/C	0.2	170	4	8	90.82
2	Pd/SBA-15	0.1	170	4	8	72.91
3	Pd/SBA-15	0.2	170	4	8	88.10
4	Pd/SBA-15	0.2	170	6	8	97.13
5	Ru/C	0.2	170	4	8	100
6	Ru/C	0.1	170	4	4	90.58
7	Ru/C	0.1	120	4	4	24.81
8	Ru/SBA-15	0.1	120	4	4	100

^aReaction conditions: eugenol (1.00 g, 6.03 mmol), *i*-PrOH (25 mL), and reaction mixture stirred at 1000 rpm.

SBA-15 was excellent compared with that of commercial Ru/C. One possible reason for the high catalytic activity of Ru/SBA-15 could be the effect of the unique mesoporous structure and uniform hexagonal channels of SBA-15. Additionally, the crystal size of self-prepared Ru/SBA-15 (2.2 nm) may be more suitable for hydrogenation than that of Ru/C (2.7 nm).

By employing *i*-PrOH as solvent and Ru/SBA-15 as catalyst, more moderate conversion conditions could be possible. As shown in Table 3, eugenol can be completely hydrotreated at

Table 3. Screen the Reaction Condition^a

entry	T/°C	t/h	catalyst/g	conv./%
1	170	4	0.2	100
2	170	8	0.1	100
3	120	8	0.1	100
4	120	4	0.1	100
5	120 ^b	4	0.1	100
6	100	4	0.1	86.79
7	80	4	0.1	29.39

^aReaction conditions: eugenol (1.00 g, 6.03 mmol), 5 wt % Ru/SBA-15, *i*-PrOH (25 mL), 4 MPa H_2 , reaction mixture stirred at 1000 rpm.

^bThe catalyst has been used once.

120 °C and in 4 MPa H_2 for 4 h with Ru/SBA-15 as catalyst. To test catalyst stability, a batch of Ru/SBA-15 catalyst was used for a second run in the eugenol hydrogenation at the same condition. A complete conversion was also obtained with the recycled catalyst (Table 3, Entry 5). The catalyst was used for two runs without further testing.

3.2. Study of Simulated Bio-oil. Simulated bio-oil (2.00 g) was hydrotreated by 0.10 g of Ru/SBA-15 in *i*-PrOH. The result showed that the simulated bio-oil could be converted effectively to alcohols at 120 °C (see Figure 3 for the GC-MS product distribution). A same result can be obtained with the reused Ru/SBA-15 at the same reaction condition. There was no loss of activity after two runs.

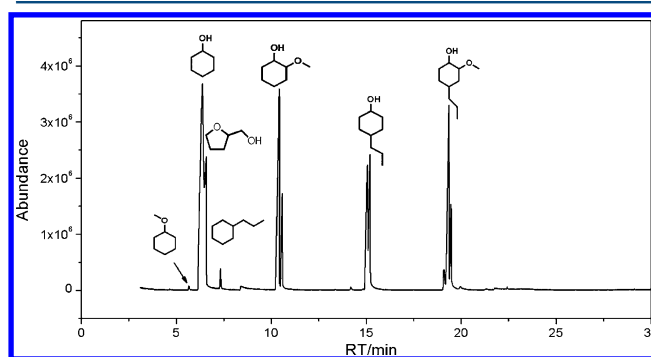


Figure 3. GC-MS spectrum after hydrogenation of simulated bio-oil. Reaction conditions: the simulated bio-oil (2.00 g), 5 wt % Ru/SBA-15 (0.10 g 4.95×10^{-2} mmol Ru), *i*-PrOH (25 mL), 4 MPa H_2 , 120 °C, and reaction mixture stirred at 1000 rpm for 4 h.

3.3. Study of Separated Bio-oil. Through glycerol-assisted distillation technology, bio-oil was separated into three fractions in our laboratory: distillate under 120 °C, distillate at 120 °C under vacuum condition, and the residues. The first fraction mainly contained about 8 wt % of acetic acid and 75 wt % of water. The second fraction mainly consisted of phenolic compounds, such as phenol, 2-methoxyphenol, 4-ethylphenol, 4-methyl-2-methoxyphenol, 4-ethyl-2-methoxy-

phenol, 4-propyl-2-methoxyphenol, 4-allyl-2-methoxyphenol, etc. and about 25 wt % of water. The residue consisted of pyrolytic lignin and glycerol. According to the above studies, the hydrogenation of the second distillate fraction of bio-oil was investigated. Distillate fraction (1.00 g) was hydrotreated at 170 °C in *i*-PrOH with 0.20 g of Ru/SBA-15 catalyst. The GC/MS of major organic components and relative contents which were expressed by peak area % are also given in Figure 4 and Table 4,

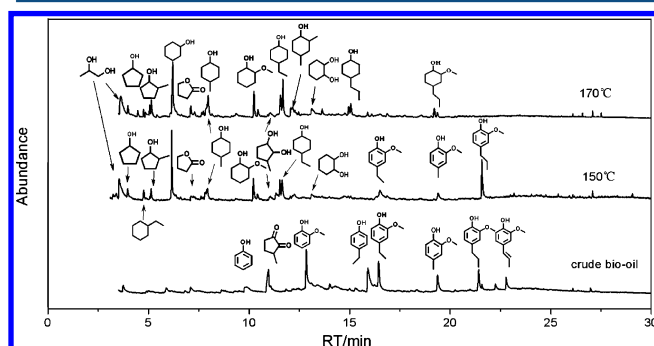


Figure 4. GC-MS spectrum before and after hydrogenation of the second fraction at 150 and 170 °C. Reaction conditions: the second fraction (1.00 g), 5 wt % Ru/SBA-15 (0.20 g 9.90×10^{-2} mmol Ru), *i*-PrOH (25 mL), 4 MPa H_2 , 170 °C, and reaction mixture stirred at 1000 rpm for 4 h.

respectively. It can be seen that, after upgrading at this condition, a series of cyclohexanol derivatives were obtained, and no phenolic compounds were detected. In addition, a small quantity of hydrocarbons were also found, such as ethylcyclohexane and propylcyclohexane; this might be attributed to the trace amount of formic acid and acetic acid existing in the distillate fraction, which served as Brønsted acid and caused hydrodeoxygenation of phenolic compounds with the cooperation of Ru/SBA-15 catalyst during the upgrading process.¹² The gas was analyzed by GC; the result showed that 0.022 g of CH_4 and a minute amount of C_2H_6 and C_3H_8 hydrocarbons were obtained (see Figure S1 in the Supporting Information). No solid products were obtained, but carbon was detected on the catalyst and the content was 8.73%. To optimize the reaction conditions, lower temperatures such as 120 and 150 °C were also investigated. The results showed that this reaction did not work effectively under lower temperatures. Take 150 °C for example, the phenol derivatives with single substituent group were hydrogenated into cyclohexanol derivatives; however, the phenol derivatives with two substituent groups, such as eugenol, could not be reduced completely (see Figure 4 and Table 4).

3.4. Catalyst Stability in Phenolic Compounds Separated from Bio-oil. To test the catalyst stability, Ru/SBA-15 was used for a second run for hydrogenation of the bio-oil fraction with phenolic compounds. Unfortunately, we were disappointed to find that the phenolic components could not be reduced. A series of tests were carried out to find out the reason of what might cause catalyst deactivation.

The XRD patterns of catalysts (Figure 2) showed that the crystal size and structure of ruthenium were not changed after bio-oil fraction upgrading, and the structure of SBA-15 was also not changed before and after upgrading (see Figure S2 in the Supporting Information). XPS was performed to identify the nature of the ruthenium nanoparticle surface. Since there was an overlap between Ru 3d and C 1s peaks at 284.6 eV, Ru 3p_{3/2}

Table 4. Major Organic Component and Relative Content of Crude Bio-oil and Upgraded Bio-oil

RT/min	name	area %		
		crude bio-oil fraction	upgraded at 150 °C	upgraded at 170 °C
alcohols				
3.629	propane-1,2-diol		10.433	10.118
3.976	cyclopentanol		3.378	1.674
5.143	2-methylcyclopentanol		2.192	5.410
6.211	cyclohexanol		13.111	15.465
7.967	4-methylcyclohexanol		6.207	7.828
10.245	2-methoxycyclohexanol		6.249	5.791
11.066	3-methylcyclopentane-1,2-diol		1.780	2.120
11.685	4-ethylcyclohexanol		8.684	12.510
12.167	2,4-dimethylcyclohexanol		3.768	6.426
13.119	cyclohexane-1,2-diol		4.935	2.365
15.061	4-propylcyclohexanol			3.882
phenols				
9.867	phenol	3.513		
10.966	3-methylcyclopentane-1,2-dione	6.839		
12.885	2-methoxyphenol	18.699		
14.029	3-ethyl-2-hydroxycyclopentanone	2.818		
15.314	2,5-dimethylphenol	2.614		
15.968	4-ethylphenol	9.731		
16.438	4-ethyl-2-methoxyphenol	7.922	6.016	
18.332	2-ethyl-6-methylphenol	1.235		
19.406	4-methyl-2-methoxyphenol	3.778	3.174	
21.409	4-propyl-2-methoxyphenol	4.443	8.540	
22.799	2-methoxy-4-(prop-1-enyl)phenol	6.008		
others				
3.277	propanoic acid	2.167	3.127	
3.382	isopropyl propionate			5.741
3.746	1-hydroxy-2-butanone	1.555		
4.845	ethylcyclohexane		2.138	1.738
5.005	2-cyclopenten-1-one	1.511		
6.854	1-butanol-2-methylene	0.564		
7.134	butyrolactone	3.766	1.224	1.887

was adopted for comparison. The Ru 3p_{3/2} signals of the fresh Ru/SBA-15 (sample a), Ru/SBA-15 regenerated from the hydrogenation of simulated bio-oil (sample b), and Ru/SBA-15 regenerated from the hydrogenation of bio-oil fraction (sample c, deactivated catalyst) were obtained and deconvoluted, as shown in Figure 5. The peaks of the Ru 3p_{3/2} binding energy at about 461.3 and 462.8 eV corresponded to the Ru⁰ and Ru (IV), respectively.^{25,26} According to literature,²⁵ the peak at about 465.4 eV is attributed to the presence of RuO_xCl_y species, most likely with Ru (IV). The presence of Ruⁿ⁺ species is due to the incomplete reduction of Ru precursors in preparation of catalyst and partial oxidation for exposure to the air. More Ru⁰ is obtained after the hydrogenation reaction. Ru⁰ acted as the primary role in the hydrogenation reaction of phenol derivatives. The XPS of the sample c is similar as that of sample b, which did not lose activity after reaction. Therefore, the reduction of Ruⁿ⁺ species is not the reason for catalytic deactivation.

The interaction between organics and Ru/SBA-15 could be the reason that caused the catalyst deactivation. Considering

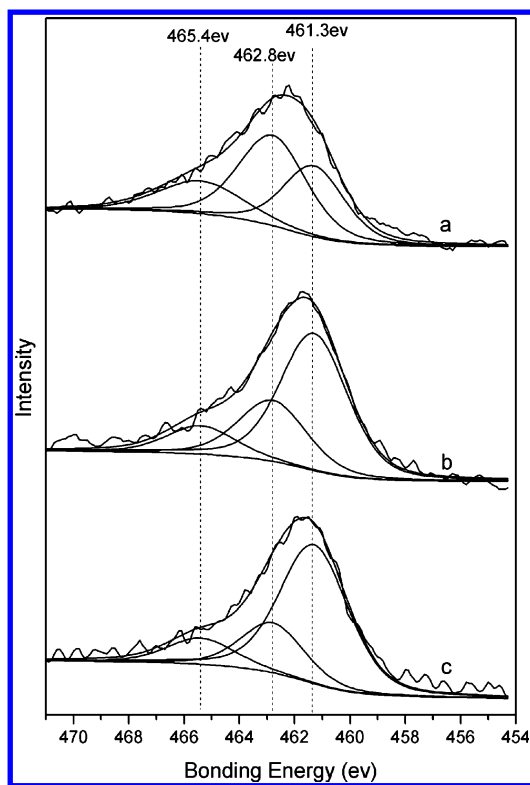


Figure 5. Ru 3p core level spectra for catalysts: (a) fresh Ru/SBA-15, (b) Ru/SBA-15 regenerated from the hydrogenation of simulated bio-oil, and (c) Ru/SBA-15 regenerated from the hydrogenation of bio-oil fraction.

that bio-oil was a complicated system, the deactivation of catalyst might be caused by the formation of coke or tar.

The BET surface area and average pore volume of catalysts are given in Table 5. From Table 5, it can be seen that, after

Table 5. Textural Properties and of Catalysts^a

sample	BET surface area (m ² /g)	average pore volume (cm ³ /g)
a	518.82	0.74
b	462.42	0.51
c	421.28	0.43

^a(a) fresh Ru/SBA-15, (b) Ru/SBA-15 regenerated from the hydrogenation of simulated bio-oil, and (c) Ru/SBA-15 regenerated from the hydrogenation of bio-oil fraction.

being used in bio-oil fraction, the BET surface area and average pore volume of Ru/SBA-15 evidently decreased, which should be due to the occupation of coke or tar in pore channels, which may cover the active site of the catalyst.

The thermogravimetric behaviors of the fresh and regenerated catalysts were analyzed. The experimental data of the TGA and DTA are presented in Figure 6. It can be seen that there was a weight gain for sample c at about 280 °C, which should not be caused by the oxidation of Ru, since no weight gain was presented for both samples b and c. It could be attributed to the oxidation of coke or complicated compounds deposited on sample c, and there was about 4.9% weight loss between 280 to 490 °C, which was in accordance with the broad exothermic peak at the same temperature range. It should be the decomposition of coke or complicated compounds deposited on the sample c.

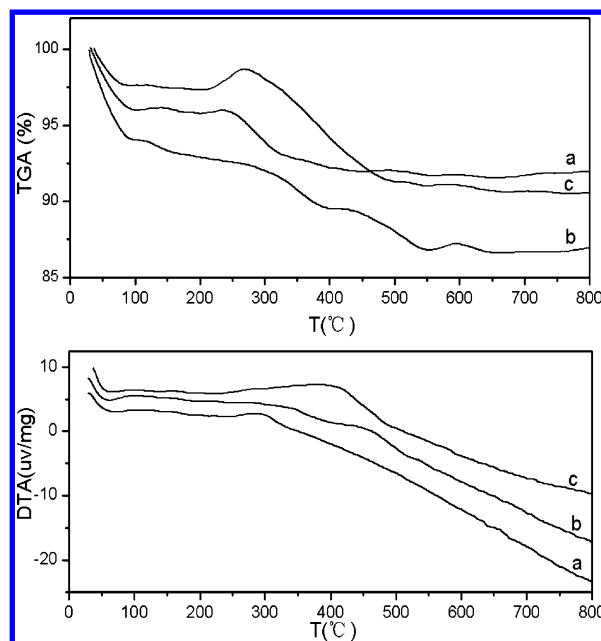


Figure 6. TGA and DTA curves of catalysts in air: (a) fresh Ru/SBA-15, (b) Ru/SBA-15 regenerated from the hydrogenation of simulated bio-oil, and (c) Ru/SBA-15 regenerated from the hydrogenation of bio-oil fraction.

4. CONCLUSION

In conclusion, components in bio-oil are super complicated and much more difficult to handle than model compounds. In this study, we developed an effective route for hydrotreating phenolic compounds separated from bio-oil to alcohols. Self-prepared catalyst of Ru/SBA-15 in combination with the solvent of *i*-PrOH can completely convert phenolic compounds into cyclohexanol and its derivatives under mild conditions. The components in simulated bio-oil did not cause Ru/SBA-15 deactivation during hydrogenation, but certain organic compounds in bio-oil did. The mechanism on catalyst deactivation could be due to the irreversible occupation of coke or tar in pore channels, which may cover the active site of the catalyst.

■ ASSOCIATED CONTENT

Supporting Information

Two figures (GC spectrum of gas obtained from hydrogenation of eugenol and XRD patterns of Ru/SBA-15). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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