

## Electronic Supplementary Information

# Low temperature catalytic Hydrogenation of Lignin-Derived Phenols to cyclohexanols over Ru/SBA-15 Catalyst

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## Experimental

### Catalyst characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were measured in a TECNAI G2-20 TWIN (FEI Co., German) instrument with an acceleration voltage of 200 kV to analyze the dispersity and crystal orientation of Ru species. The samples were dispersed in ethanol by ultrasonication and dropped onto copper grids for observation. The particle diameter (d) of Ru particles were counted by the software of Nano Measurer.

N<sub>2</sub> adsorption-desorption isotherms were collected with a Micromeritics Tristar II 3020 analyzer to analyze the surface areas and the pore volumes of the catalyst samples. The surface areas and pore volumes were determined by the Brunauer-Emmett-Teller (BET) Barrett-Joyner-Halenda (BJH) equation, respectively. Before analysis, the samples were heated at 120 °C and 300 °C for 2 h under vacuum, respectively.

Powder X-ray diffraction (XRD) were obtained using a Shimadzu XRD-6100 diffractometer with Cu-K $\alpha$  monochromatized radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 30 mA to analyze the crystalline phase of the catalysts. The scanning angle were recorded over the  $2\theta$  range of 5–80 ° at a scan rate of 5 ° min<sup>-1</sup>.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS Ultra DLD (KRATOS) spectrometer with a monochromatic Al-K $\alpha$  X-ray source to analyze the chemical state of supported metals. The binding energy was internally calibrated by setting the C1s peak at 284.8 eV.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was

performed by a Thermo Elemental IRIS Advantage ER/S spectrometer (Thermo Elemental, MA, USA) to measure the actual metal loading of the catalysts. The samples were dissolved in aqua regia and HF, then diluted with deionized water before measurement.

Thermogravimetric analysis (TG) was used to identify the coke deposition on the used catalysts by a NETZSCH STA 449 F5 analyzer. About 0.01 g sample was placed in an alumina crucible with a platinum crucible cover. The sample was heated to 800 °C with 10 °C min<sup>-1</sup> under 60 mL min<sup>-1</sup> dry air flow.

### **Catalytic tests**

The hydrogenation of lignin-derived phenols was performed in a 100 mL Parr reactor. In a typical reaction, 5 mmol substrate with 0.2 g of Ru/SBA-15 and 50 mL water were loaded in the reactor, which was flushed with N<sub>2</sub> for 3 times, and finally filled with 2 MPa H<sub>2</sub> for reaction. Then the reactor was set to desired temperature with stirring at 400 rotation per minute. The reaction was performed for scheduled time and then cooled down by fan for about 20 min to room temperature. After filtration, the fluid was analyzed qualitatively and quantitatively by GC-MS (Agilent 6820) and GC-FID (PERKINELMER Clarus 580) for yield calculation. A DB-5 capillary column (30 m × 0.25 mm × 0.25 μm) was used both in GC and GC-MS, and the temperature program was set as rising with a ramp of 5 °C min<sup>-1</sup> from 50 °C to 200 °C and maintaining for 5 min. For the GC-FID instrument, the flow rate of nitrogen was 1 mL min<sup>-1</sup>, the injector temperature was 280 °C and the detector temperature was set at 330 °C mainly to ensure that the sample could be completely vaporized to avoid the contamination of the

detector. Acetophenone was used as internal standard.

**Table S1** Hydrodeoxygenation (HDO) selectivity of lignin-derived phenols in literature and this work.

Entry	catalyst	reactant	solvent	Reaction conditions (T, t, P)			Conv. (%)	Selectivity <sup>a</sup>				Ref.
				T/°C	t/h	P/MPa		RCol	RCone	RCane	RPh	
1	Rh-H	phenol	H <sub>2</sub> O	30	6	5	100	100				1
2	Pd/γ-Al <sub>2</sub> O <sub>3</sub>	phenol	H <sub>2</sub> O	60	12	2	100	100				2
3	Pd-HAP	phenol	H <sub>2</sub> O	75	3	1	100		100			3
4	Pd@mpg-C <sub>3</sub> N <sub>4</sub>	phenol	H <sub>2</sub> O	45	12	0.1	99		98.5			4
5	Pd/C+AlCl <sub>3</sub>	phenol	CH <sub>2</sub> Cl <sub>2</sub>	30	12	1	>99.9		99.9			5
6	Ru/5Nb <sub>2</sub> O <sub>5</sub> -5MC	phenol	H <sub>2</sub> O/decalin	200	4	1	100			100		6
7	Ru/SBA-15	phenol	H <sub>2</sub> O	20	5	2	>99.9	100				This study
8 <sup>b</sup>	Ru/C	G	acetic acid	80	4	3	24	25				7
9	RuZrLa-2	G	H <sub>2</sub> O	160	4	4	100	81				8
10	Ru-MnO <sub>x</sub> /C	G	H <sub>2</sub> O	160	2	1.5	99.9	79				9
11 <sup>c</sup>	NiRu-HT	AG	isopropanol	150	6	2.5	100	83.8				10
12 <sup>d</sup>	Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	PG	hexadecane	250	0.5	1	100	85				11
13	Ni/Beta	G	-	300	-	4	100			76		12
14	Ru/HZSM-5-OM	AG	H <sub>2</sub> O	170	4	4	>99.5			83		13
15	Au/TiO <sub>2</sub> +HZSM-5	PG	benzene	350	2	10	100				60	14
16	Ru/SBA-15	AG	H <sub>2</sub> O	80	4	2	>99.9	37.4				This study

<sup>a</sup> 4-alkylcyclohexanol (RCol), 4-alkylcyclohexanone (RCone), 4-alkylcyclohexane (RCane), 4-alkylphenol (RPh); <sup>b</sup> guaiacol (G); <sup>c</sup> 4-allylguaiacol (AG); <sup>d</sup> 4-propylguaiacol (PG).

**Table S2** Ru particle diameter ( $d_{\text{XRD}}$ ) calculated by Ru(101) in XRD patterns.

Catalyst	$\beta$ (FWHM)	$2\theta$	$d_{\text{XRD}}$ (nm) <sup>a</sup>
1 wt.% Ru/SBA-15	0.465	43.756	18.21
3 wt.% Ru/SBA-15	0.539	43.739	15.71
5 wt.% Ru/SBA-15	0.759	43.958	11.17
7wt.% Ru/SBA-15	0.607	43.838	13.96

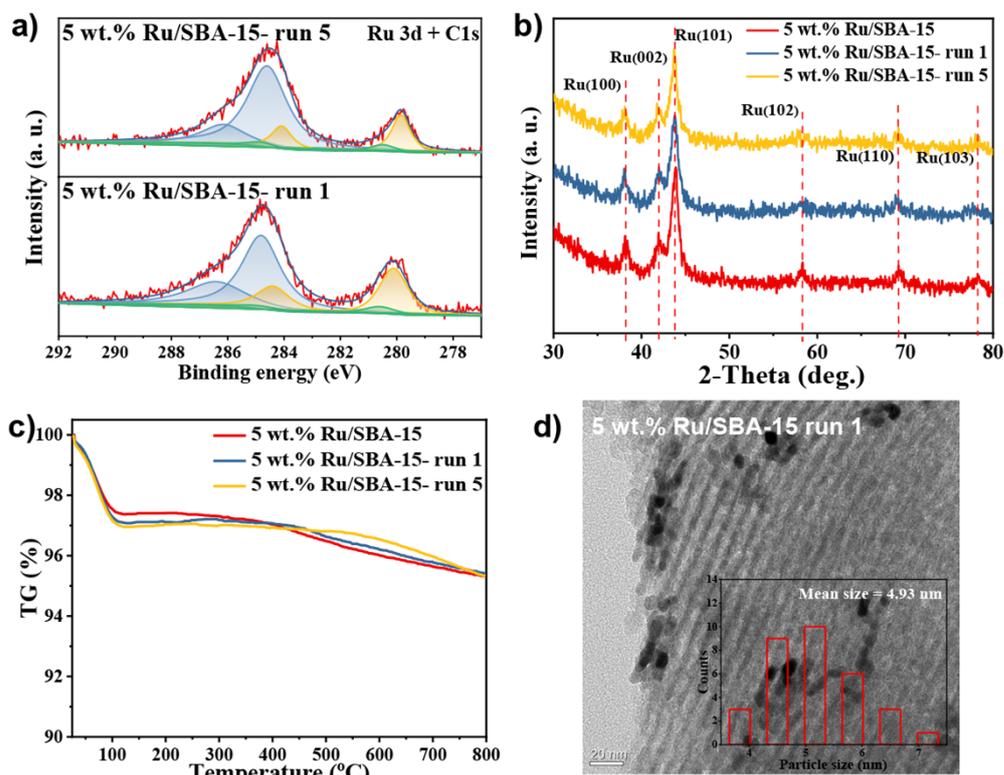
<sup>a</sup>  $d_{\text{XRD}} = K\lambda / (\beta \cos\theta)$ , where K is constant (0.89),  $\lambda$  is the wavelength of X-rays (0.15406).

**Table S3** Specific binding energies of Ru 3d of Ru/SBA-15 catalysts.

Sample	Name	Position (eV)	Area	FWHM (eV)	%Cont	Ru <sup>0</sup> / (Ru <sup>0</sup> + Ru <sup>δ+</sup> )
1 wt.% Ru/SBA-15	Ru <sup>0</sup> 3d <sub>5/2</sub>	279.60	37.55	1.75	54.7	91.2
	Ru <sup>0</sup> 3d <sub>3/2</sub>	284.16	25.04	0.67	36.5	
	Ru <sup>δ+</sup> 3d <sub>5/2</sub>	280.60	3.63	1.20	5.3	
	Ru <sup>δ+</sup> 3d <sub>3/2</sub>	285.17	2.42	0.75	3.5	
3 wt.% Ru/SBA-15	Ru <sup>0</sup> 3d <sub>5/2</sub>	279.70	91.14	0.94	50.3	83.9
	Ru <sup>0</sup> 3d <sub>3/2</sub>	283.95	60.76	1.13	33.5	
	Ru <sup>δ+</sup> 3d <sub>5/2</sub>	280.80	17.55	0.90	9.7	
	Ru <sup>δ+</sup> 3d <sub>3/2</sub>	284.95	11.70	0.53	6.5	
5 wt.% Ru/SBA-15	Ru <sup>0</sup> 3d <sub>5/2</sub>	279.90	97.01	0.95	52.2	87.0
	Ru <sup>0</sup> 3d <sub>3/2</sub>	284.20	64.67	1.31	34.8	
	Ru <sup>δ+</sup> 3d <sub>5/2</sub>	280.60	14.50	0.75	7.8	
	Ru <sup>δ+</sup> 3d <sub>3/2</sub>	284.80	9.67	1.03	5.2	
7 wt.% Ru/SBA-15	Ru <sup>0</sup> 3d <sub>5/2</sub>	279.80	119.64	1.00	50.1	83.6
	Ru <sup>0</sup> 3d <sub>3/2</sub>	284.07	79.76	1.25	33.4	
	Ru <sup>δ+</sup> 3d <sub>5/2</sub>	280.81	23.50	1.00	9.9	
	Ru <sup>δ+</sup> 3d <sub>3/2</sub>	284.99	15.68	1.20	6.6	

**Table S4** Specific binding energies of Ru 3d of used Ru/SBA-15 catalysts.

Sample	Name	Position (eV)	Area	FWHM (eV)	%Cont	Ru <sup>0</sup> / (Ru <sup>0</sup> + Ru <sup>δ+</sup> )
5 wt.% Ru/SBA-15- run 1	Ru <sup>0</sup> 3d <sub>5/2</sub>	280.11	515.59	1.20	51.0	84.9
	Ru <sup>0</sup> 3d <sub>3/2</sub>	284.39	343.73	1.40	34.0	
	Ru <sup>δ+</sup> 3d <sub>5/2</sub>	280.60	91.42	1.30	9.0	
	Ru <sup>δ+</sup> 3d <sub>3/2</sub>	284.88	60.95	1.98	6.0	
5 wt.% Ru/SBA-15- run 5	Ru <sup>0</sup> 3d <sub>5/2</sub>	279.85	295.25	0.78	51.1	85.2
	Ru <sup>0</sup> 3d <sub>3/2</sub>	284.09	196.83	0.86	34.1	
	Ru <sup>δ+</sup> 3d <sub>5/2</sub>	280.50	69.35	1.04	12.0	
	Ru <sup>δ+</sup> 3d <sub>3/2</sub>	284.85	16.23	1.07	2.8	



**Figure S1** a) XRD<sup>a</sup>, b) XPS<sup>b</sup>, c) TG<sup>c</sup> and d) TEM<sup>d</sup> data of the used Ru/SBA-15 catalysts.

<sup>a</sup> The specific binding energy of used 5 wt.% Ru/SBA-15 showed in Table S2 indicated that the Ru<sup>0</sup> content (~85%) of the used catalysts had no obvious decrease compared with the fresh catalyst (87.0%).

<sup>b</sup> The characteristic diffraction peaks of Ru<sup>0</sup> observed in XRD patterns of the used catalysts was the same with the fresh sample.

<sup>c</sup> The weight loss at about 100 °C might be attributed to water, and there was no other form of weightlessness both in the fresh and used catalysts.

<sup>d</sup> The particle diameter of the used 5 wt.% Ru/SBA-15 catalyst showed no increase compared with the fresh sample with the mean size of 4.93 nm, and there was no obvious agglomeration, which could account for the high activity and stability of the catalyst in the aqueous system.

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