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Electronic Supplementary Information

Continuous hydrogenolysis of acetal-stabilized lignin in flow

Wu Lan, Yuan Peng Du, Songlan Sun, Jean Behaghel de Bueren, Florent Héroguel, Jeremy S. Luterbacher

Laboratory of Sustainable and Catalytic Processing, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Station 6, 1015 Lausanne, Switzerland.

jeremy.luterbacher@epfl.ch

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S1. Materials and chemicals

Commercially available compounds were purchased and used as received unless stated otherwise. Dioxane (99.8%) was purchased from ABCR. Sodium bicarbonate (99%), active carbon, nickel (Ⅱ) nitrate hexahydrate (99.999%), ethyl acetate (99.8%), diethyl ether (99%), methanol (99.9%), hexane (99.9%), decane (99.9%), and Ru/C (5 wt%) were purchased from Sigma-Aldrich. Propionaldehyde (99%) hydrochloride acid (37%), nitric acid (65%) was purchased from VWR. Hydrogen (99.999%), helium (99.999%), and nitrogen (99.999%) were obtained from Carbagas.

Birch (Betula pendula) particles were provided by M. Studer from Applied Sciences, Bern University at a particle size <0.5 cm. The Klason lignin content was analyzed according to the NREL (National renewable energy laboratory, U.S.A.) standard procedure [1].Generally, 300 mg of dried, extractives-free birch and 3 mL of 72% sulfuric acid was added to a 25 mL Erlenmeyer flask, which is placed in a water bath set at 30 °C. After 1 h, the mixture was transferred to a 250 mL glass bottle and 84 mL of water was added to dilute the acid concentration to 4%. The glass bottle with a securely screwed Teflon cap was then put in an autoclave (Tuttnauer Schweiz) and held at 121 °C for 1 h. After the vessel cooled down to room temperature, the residue was collected by filtration and washed with distilled water to remove the acid. The residue was dried at 110 °C for 24 h and then its weight was measured. The experiment was conducted in triplicate and the average values were used.

S2. Lignin preparation

The propylidene acetal-protected lignin was extracted as described in our previous work [2-3]. Generally, 40.0 g birch, 36 mL propionaldehyde, 200 mL 1,4-dioxane and 6.8 mL HCl (37 wt%) were introduced in a round bottom flask. The flask was put in an oil bath set at 85 °C for 3 hours under reflux. After cooling the system down to room temperature, 13.0 g $NaHCO_3$ was added and the solution was stirred for 6 h until the solution was neutralized. The reaction mixture was then filtered and the filter cake was washed with an additional 100 ml dioxane. The resulting solution was then concentrated at 45 °C under reduced pressure. The resulting dark brown oil was diluted with 50-80 mL EtOAc. The lignin was then precipitated by adding the solution dropwise to 1500 mL hexane while under intense stirring. The precipitated lignin was collected by centrifugation and then washed with hexane (150 mL×2) and diethyl ether (150 mL×2) to eliminate any residual sugars. The recovered lignin was dried at room temperature in a desiccator for 24 h. The final mass of the precipitated powder was around 9.0 g.

S3. Hydrogenolysis of lignin in continuous flow reactor

Hydrogenolysis of the propylidene acetal-protected lignin was performed with a custom-built continuous flow reactor system. The tubes, valves, and pressure gauges were purchased from Swagelok (U.S.A). A quarter inch tube with 40-42 cm in length was used as the reactor. 125-500 mg of catalyst (5wt% Ni/C or 5wt% Ru/C) were mixed with 3.0-3.6 g of fused crushed silicon dioxide (0.125 mm<d<0.25 mm) to create a catalyst bed in the tube of about 17~18 cm, which corresponded to the zone in contact with the heater. Silicon carbide or silicon dioxide was used to fill the two ends of the tube and quartz wool was used to plug the reactor and delimitate each section (Figure S1).

Figure S1. Schematic diagram of tube packing for continuous hydrogenolysis.

The reactor was placed within a vertical split furnace and a K-type thermocouple measured the reaction temperature, which was controlled by a PID temperature controller (Omega CN7800). Before lignin hydrogenolysis, the catalyst was reduced *in situ* at 300 °C for 5 h achieved with a 2 °C/min ramping rate. The reaction temperature was then set to 180 °C. The feedstock that was used consisted of the protected lignin in a dioxane/methanol solution (2:8, v/v) at a concentration of 2.5 mg/mL or 5.0 mg/mL. The solution was filtered to eliminate any potential precipitate before the reaction to avoid clogging issue during the process. The feed was continuously introduced into the reactor by a HPLC pump set at 0.1-0.4 mL/min, depending on the desired weight hourly space velocity (WHSV). The flow rate of H_2 was set at 50 mL/min by a mass flow controller (Brooks Instrument, U.S.A) and the pressure was set by a back pressure regulator (TESCOM, Vordruckregler Serie 26-1700, U.S.A) at 60 bar. A sample collector (with a maximum volume of about 100 mL) with a needle valve was connected after the reactor. Samples were taken every 2-4 h during the reaction for GC-FID analysis. The WHSV was calculated using the following equation; where c_{feed} is the lignin concentration of the feedstock solution; v_{feed} is the flow rate of the feedstock solution; $m_{cata.}$is the mass of catalyst used in the reaction.

$$\mathrm{WHSV} = \frac{c_{feed} \times v_{feed}}{m_{cata.}} \quad (1)$$

The turnover number (TON) and turnover frequency (TOF) in terms of monophenolic monomer yield were calculated using the following equation, in which $n_{monomer}$ is the number of moles of monopheenolic monomers produced; $n_{active\ sites}$ is the number of moles of surface metal sites on the catalyst determined by H_2 chemisorption (see Section 6.2); t is the reaction duration..

$$\mathrm{TON} = \frac{n_{monomer}}{n_{active\ sites}} \ (2); \ \ \mathrm{TOF} = \frac{n_{monomer}}{n_{active\ sites} \times t} \ (3)$$

S4. Batch Hydrogenolysis of lignin

200 mg protected lignin, 50 mg supported catalyst, and 20 mL methanol were added into a 50 mL high-pressure Parr reactor (stainless steel) with a magnetic stirred bar. The reactor was placed on a hot plate equipped with magnetic stirring and a heating block connected to a variable power supply controlled by a PID temperature controller (Omega CN7800). A K-type thermocouple measured the reaction temperature through a thermowell. Once sealed, the reactor was purged with H_2 3 times to expel air, and then pressurized to 40 bar at room temperature again with H_2. After that, the reactor was heated up to 200 °C and kept at this temperature for 15 h under continuous stirring (400 rpm). After the reaction, the reactor was cooled down to room temperature using a stream of compressed air. The reaction mixture was filtered using a PFTE syringe filter and 1 mL of the solution was sampled for analysis.

S5. Qualification and quantitation of monomers

Qualitative analysis of the lignin hydrogenolysis products was performed on Agilent 7890B series GC equipped with an HP5-MS capillary column and an Agilent 5977A series mass spectroscopy detector. The injection temperature was 300 °C. 1 μL of sample was injected with an autosampler in split mode (split ratio: 25:1). The column was initially kept at 40 °C for 3 min, then was heated at a rate of 30 °C/min to 100 °C, followed by a heating rate of 40 °C/min to 300 °C and held for 5 min.

Quantitative analysis of the generated monophenolic monomers was performed using an Agilent 7890B series GC equipped with an HP5-column and a flame ionization detector (FID). The temperature ramping program for the GC-FID was the same as that of the GC-MS. Sensitivity factors of the products were obtained by using estimates based on the effective carbon number (ECN). Yield calculations were performed as described in our pervious report [4].

S6. Catalyst characterization

S6.1 N_2 physisorption

Brunauer-Emmett-Teller (BET) surface areas and Barrett-Joyner-Halenda (BJH) mesoporous volumes were calculated from N_2 physisorption measurements performed with a Micromeritics 3Flex apparatus. Around 100 mg samples were loaded into the cell and dried under vacuum ($<10^{-3}$ mbar) at 120 °C overnight. The measurements were performed at liquid nitrogen temperature between 10^{-5} and 0.99 relative N_2 pressure. The BET surface area and BJH mesoporous volume were calculated using the equipment software (3Flex Version 5.01) without further parameter modification.

S6.2 H_2 chemisorption

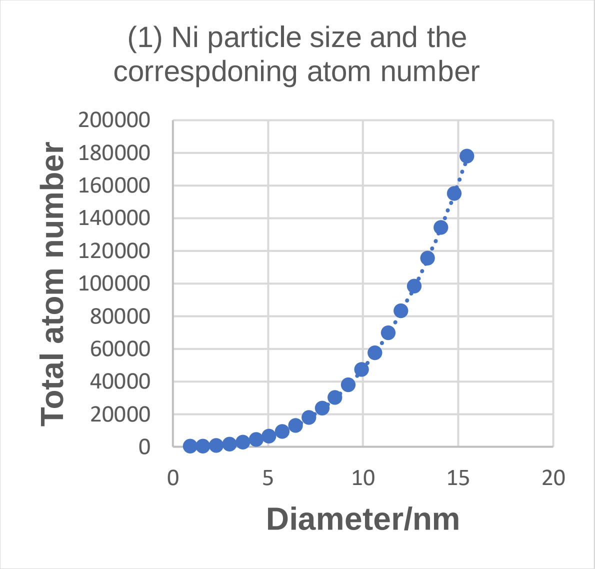
The H_2 chemisorption was also performed on the Micromeritics 3Flex using a U-type cell. Typically, 50-150 mg catalyst was added into a cell with quartz wool. After loading the instrument, the catalyst was pretreated under H_2 at 450 °C for 2 h using a heating rate of 5 °C/min. The quantity of H_2 absorbed on the catalysis was measured at 0-450 mmHg (absolute pressure). Assuming the metal catalyst contain a strong and a weak binding site to H_2, a dual Langmuir equation (4) was used for curve fitting and the Langmuir parameters were calculated in Matlab. The Q_{total} value (5) was used to calculate the active site and metal dispersion of the catalyst. Accessible Ni and Ru sites were quantified by assuming a 2:1 stoichiometry between metal and adsorbed H_2. In the equations, Q_s and Q_w represent the quantity of absorbed H_2 on the strong and weak sites of the catalyst; k_s and k_w represent the absorption rate constants for the catalyst's strong and weak adorption sites, respectively; Q_{total} represents the sum of absorbed H_2 quantity on strong and weak site of the catalyst.

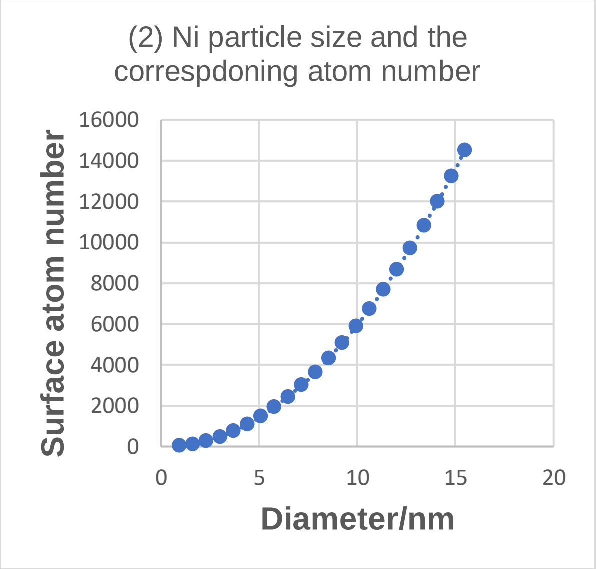
$$\mathrm{f}(x) = Q_s \times k_s \times \frac{x}{1+x\times k_s} + Q_w \times k_w \times \frac{x}{1+x\times k_w} \quad (4)$$

$$Q_{total} = Q_s + Q_w \quad (5)$$

S6.3 Transmission electron microscopy (TEM)

The catalyst's morphology was characterized using Transmission Electron Microscopy (TEM) and High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) on a FEI Talos with 200 kV acceleration voltage in the mode resulting in atomic number contrast (Z contrast). Lacey carbon grids were prepared by directly ''dipping'' the grid into the sample powder. Energy-Dispersive X-ray spectroscopy (EDXS) analysis was performed using Bruker Esprit software. The particle size distribution was estimated by statistical analysis of at least 200 measurements. Metal dispersion (defined as ratio between surface and total metal atoms) was calculated back from particle size distribution using the truncated cubic octahedron model to sum the surface and bulk metal atoms of all individual particles counted from TEM images.[5] The curves and formulas used to calculate total and surface atom number are shown in the following figures.





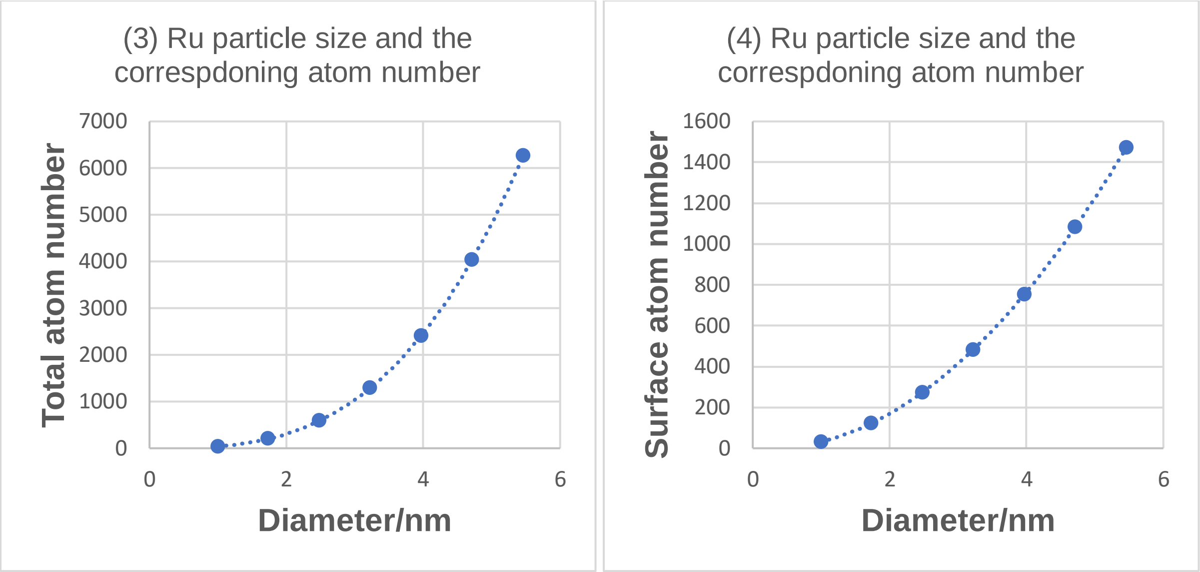


Figure S2. Fitting curves of the diameter of metal nanoparticle size and the corresponding total atom number and surface atom number. The equations of the curves are showed as followed, in which $M_{total.Ni}$ and $M_{total.Ru}$ represent the total atom number of a single particle of Ni and Ru, respectively; $M_{surface.Ni}$ and $M_{surface.Ru}$ represent the surface atom number of Ni and Ru particles, respectively; d represents the particle diameter.

$$M_{total.Ni} = 47.7890d^3 + 0.8381d^2 - 6.3761d + 8.8441 \quad (6)$$

$$M_{surface.Ni} = 62.2580d^2 - 27.1800d + 3.4229 \quad (7)$$

$$M_{total.Ru} = 38.0185d^3 + 4.4929d^2 - 11.3817d + 7.9498 \quad (8)$$

$$M_{surface.Ru} = 53.8249d^2 - 24.7518d + 3.0877 \quad (9)$$

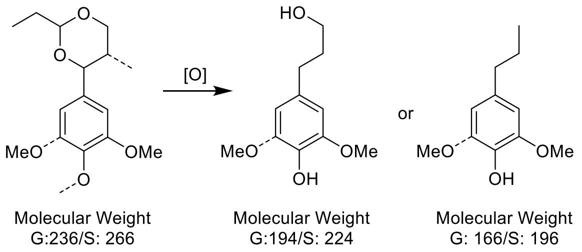
S6.4 Inductively coupled plasma - optical emission spectrometry (ICP-OES)

The metal content of the catalyst and the liquor produced by hydrogenolysis was measured on an Agilent 5110 ICP-OES system. The catalyst (~10 mg) was first digested in 2 mL aqua regia (37% HCl:65% HNO_3, 3:1, v/v) at room temperature for 2 h. The collected hydrogenolysis liquor was first concentrated under reduced pressure in a rotavap. 25 mL aqua regia was partially introduced to the leftover oil by 3 times and digested for 5 h. Following digestion, the mixture was transferred to a 200 mL volumetric flask. Finally, 15 mL of the solution was filtered through a syringe filter for analysis by ICP-OES.

S7. Elemental analysis of hydrogenolysis oil

The lignin hydrogenolysis oil was concentrated with a rotary evaporator and then dried using a Schlenk line overnight to completely remove the solvent. Analysis of C and H content was performed according to ASTM D 5291-02 standard[6]. Analysis of O content was performed on a Foss-Heraeus elemental analyzer CHN-O-Rapid.

S8. Estimation of the lignin oil yield



We estimated that the syringyl (S):guaiacyl (G) ratio was 8:2 and that the β–O–4 content in the isolated lignin was 60% of the total linkages using peaks integrals of the HSQC spectrum in our previously study[3]. The molecular weights of β–O–4 bonded monomeric units in native lignin is 196 g/mol for a G units and 226 g/mol for an S units. The weight loss of producing dihydrosinapyl alcohol and propylsyringol were 15.8% and 26.3%, respectively. And the mass loss associated with producing dihydroconiferyl alcohol and propylguaiacol were 17.8% and 29.7%, respectively. We also assume that every C–C linked unit loses one oxygen during hydrogenolysis (corresponding to a 5% mass loss). Therefore, the estimated maximum oil yield was calculated using the following equation, in which m_{rS} and m_{rG} are the remaining mass fraction of S and G units in β–O–4 linkage; m_{rC} is the remaining mass fraction of C–C linkages; *P_i* represents the fraction of S or G units, or β–O–4 linkages.

$$Maximum\ Oil\ yield = (m_{rS} \times P_S + m_{rG} \times P_G) \times P_{\beta-O-4} + m_{rC} \times (1 - P_{\beta-O-4}) \quad (10)$$

Therefore, if all products are propyl guaiacol and syringol, the maximum yield of lignin oil was estimated as:

$$(73.7\%\times80\%+70.3\%\times20\%)\times60\%+95\%\times40\%=81.8\%$$

On the other hand, if all products are guaiacyl or syringyl propanol, the maximum yield of lignin oil was estimated as:

$$(84.2\%\times80\%+82.2\%\times20\%)\times60\%+95\%\times40\%=88.3\%$$

We concluded that the oil yield should be in a range between 82 and 88 wt%.

S9. Assessment of mass transfer limitations under flow condition.

Mass transfer limitations were assessed using the Weisz-Prater criterion as showed in the following equation:

$$\frac{r_{obs}(R_p)^2}{D_{TA}^{e} C_{AS}} < 1 \quad (11)$$

In which: r_{obs} is the observed reaction rate, mol L^{-1} s^{-1};

R_p is the spherical particles radius, cm;

D_{TA}^{e} is the effective transition diffusivity, cm^2 s^{-1};

C_{AS} is the concentration at the surface of the catalyst particle, mol L^{-1}.

Bulk diffusivities of lignin oligomer in dioxane/methanol solution were calculated using the Wilke-Chang equation (12). Solvents dynamic viscosities μ were estimated from literature[7]. A viscosity value at 308.15 K was used for calculation instead of that at 453.15 K (reaction temperature, because of the absence of such data), leading to an underestimation of D_{AB}, and therefore, an overestimation of Weisz-Prater criterion.

$$D_{AB} = 7.4 \times 10^{-8} \frac{T}{\mu} \frac{(xM_B)^{1/2}}{V_A^{0.6}} \quad (12)$$

Parameter	Description	Unit	Value
T	absolute temperature	K	453.15
x	association parameter	-	1
M_B	molecular weight of the solvent	g mol^{-1}	43.26
μ	dynamic viscosity of the solvent	cP or mPas	0.8533
V_A	molar volume at boiling point	cm^3 mol^{-1}	57.44
D_{AB}	bulk diffusivity	cm^2 s^{-1}	2.27×10^{-5}

The internal diffusivity within the pores of the catalyst particles can be calculated from a size ratio of solute over pore diameter and the bulk diffusivity using the following equations (13 and 14) The solute diameter was calculated using the MarvinSketch software and assuming an oligomer with 10 phenylpropanoid units. Pore diameter was calculated using the BJH method on the desorption branch of the N_2 adsorption isotherm.

$$\frac{D_{AB,pore}}{D_{AB}} = (1 - \lambda)^4 \quad (13)$$

$$\lambda = \frac{d_s}{d_p} \quad (14)$$

Parameter	Description	Unit	Value
ds	solute diameter	nm	4
dp	pore diameter	nm	5
$D_{AB,pore}$	pore diffusivity	cm^2 s^{-1}	3.64×10^{-8}

The effective transition diffusivity was calculated using the porosity (ε) and the tortuosity (τ) as equation (15). In the absence of experimental data, ε and τ can be estimated as 0.5 and 4, respectively, according to Davis and Davis[8].

$$D_{TA}^{e} = D_{AB}^{e} = \frac{\varepsilon}{\tau} D_{AB,pore} \quad (15)$$

The surface concentration C_{AS} was calculated using the mass transfer coefficient k_c (16). Because $C_{AB} \gg r_{obs}^{surf}/k_c$, C_{AB} was assumed to be equal to C_{AS}, indicating no significant external mass transfer limitation was observed.

$$r_{obs}^{surf} = k_c(C_{AB} - C_{AS}) \quad (16)$$

The reaction rate was directly calculated from an extrapolated rate of the flow reaction result, which estimates the fastest reaction rate seen during the transformation (i.e. from the extrapolated TOF at zero conversion, which is calculated in Figure S5). Spherical particles radius of activated carbon was estimated as 10^{-4} cm. Therefore, the data used to calculate the Weisz-Prater criterion were listed as followed:

Parameter	Description	Unit	Value
r_{obs}	observed reaction rate	mol L^{-1} s^{-1}	1.39 10^{-6}
R_p	spherical particles radius	cm	0.0001
D_{TA}^{e}	effective transition diffusivity	cm^2 s^{-1}	4.55×10^{-9}
C_{AS}	surface concentration	mol L^{-1}	2.21×10^{-3}
	Weisz-Prater criterion	-	1.38 10^{-3}

Since the resulting Weisz-Prater criterion was several orders of magnitude below unity, we concluded that the flow hydrogenolysis of lignin under our condition was free of both internal and external mass transfer limitations.

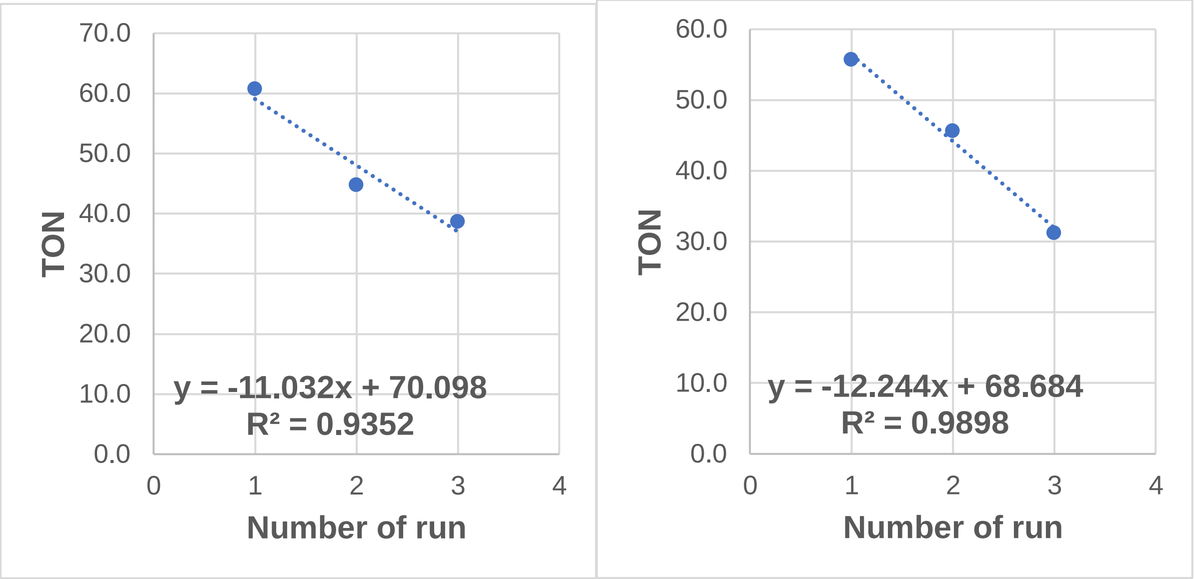


Figure S3. TON of Ni/C (left) and Ru/C (right) during lignin hydrogenolysis, which decreased with an increasing number of runs.

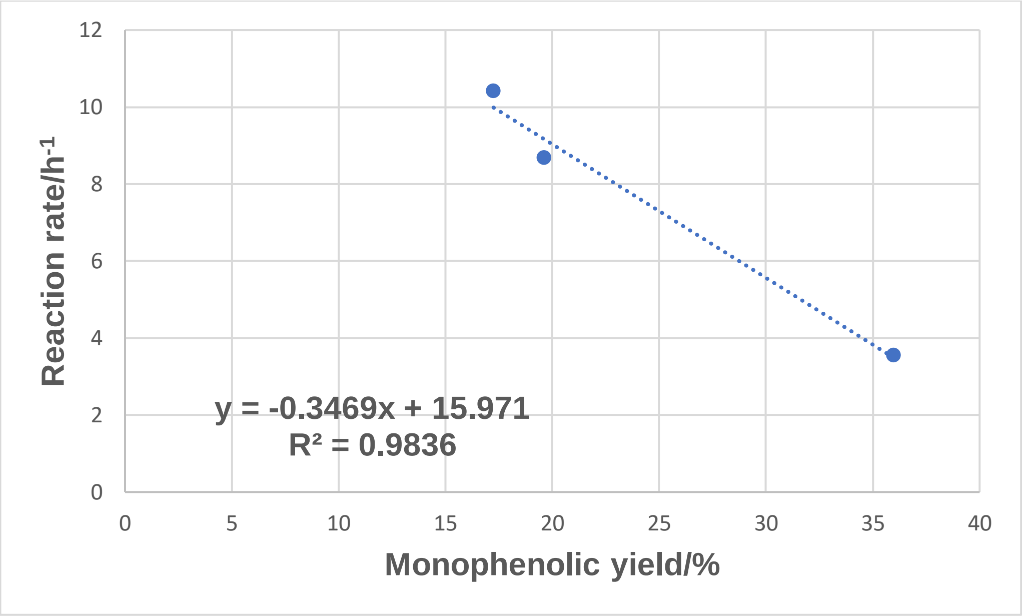


Figure S4. Plot of linear regression between the monophenolic yield and reaction rate.

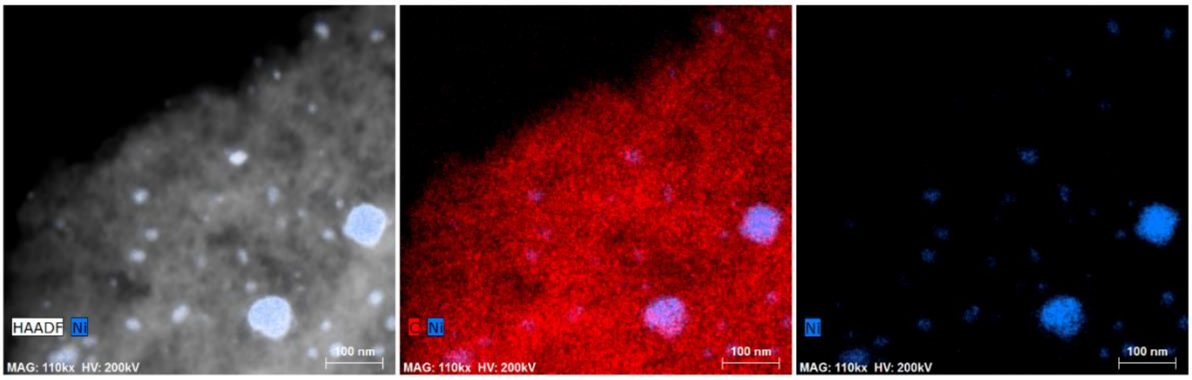


Figure S5. TEM and HADDF images of the spent Ni/C catalyst.

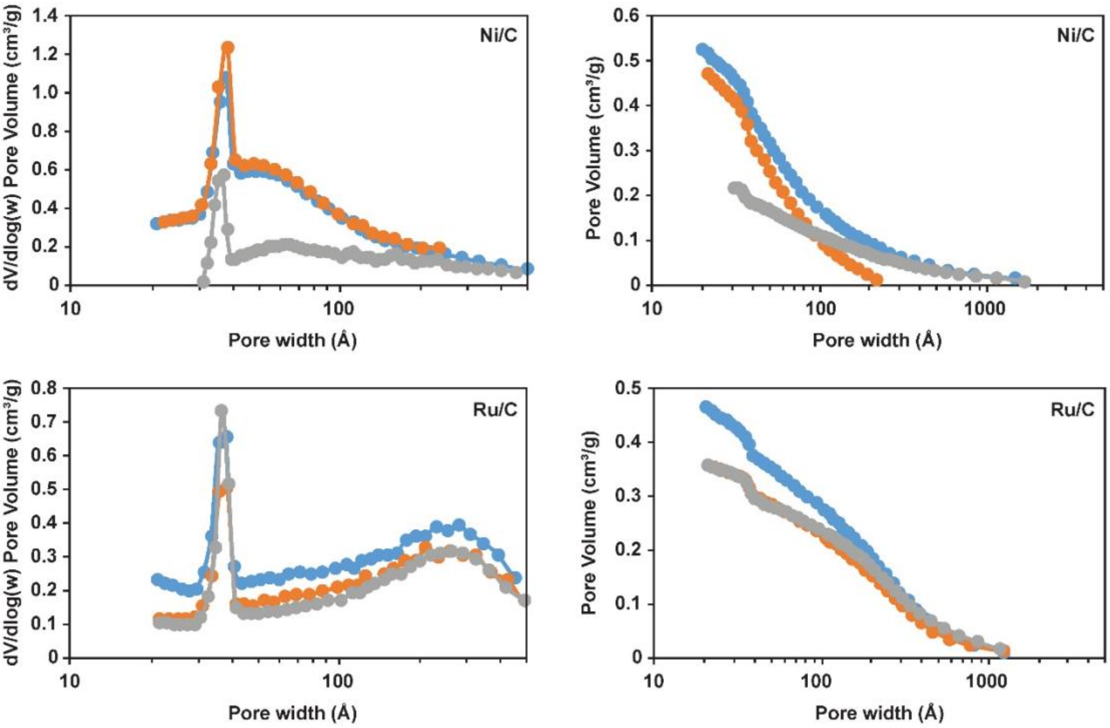


Figure S6. Pore size distribution of Ni/C and Ru/C. The blue lines represent fresh catalyst; the orange lines represent the catalyst used for 60-80 h (corresponding to the experiment in Figure 2A and 2C); the gray lines represent the catalyst used for 180-200 h (corresponding to the experiment in Figure 2B and 2D).

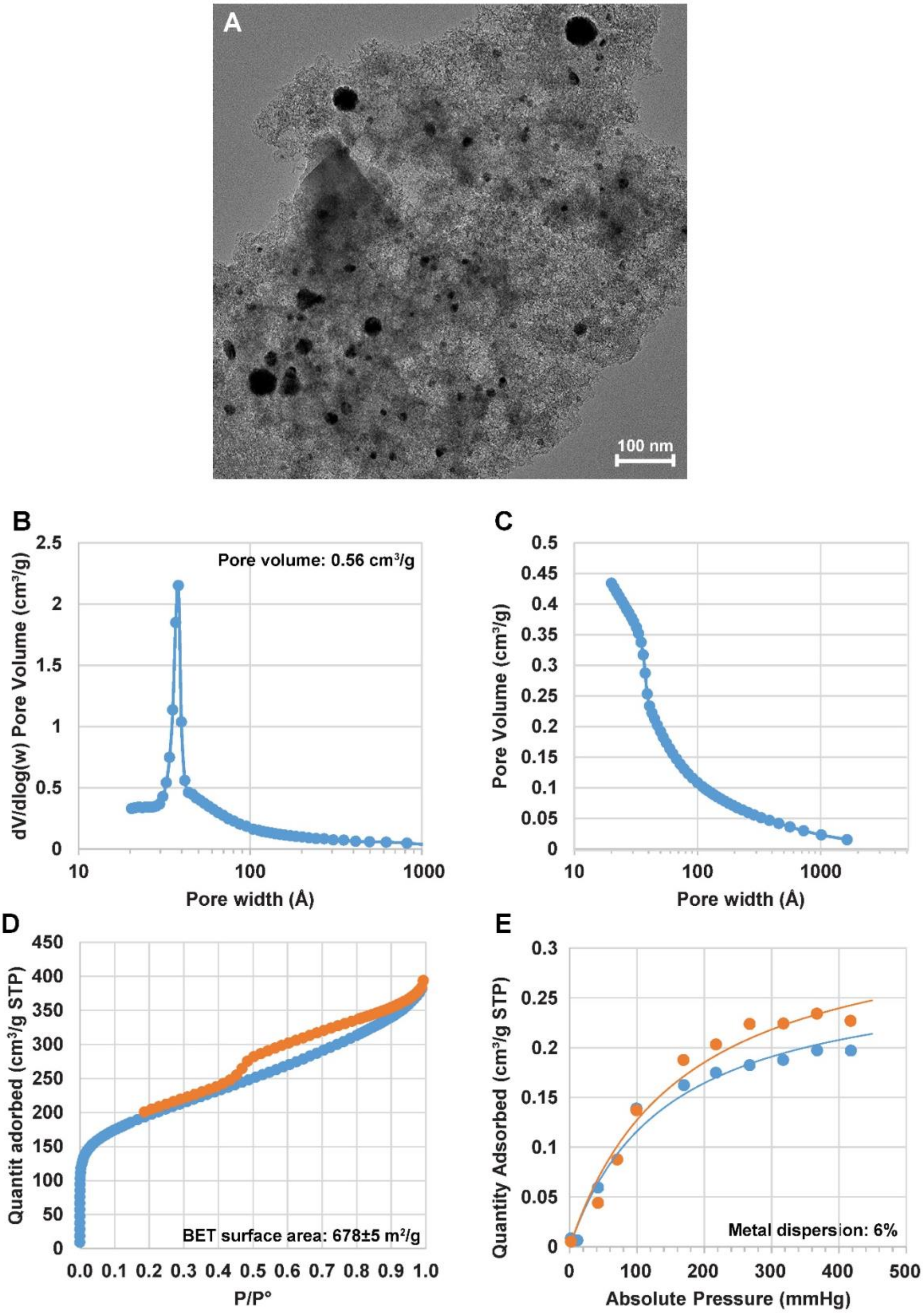


Figure S7. Characterization of the spent catalyst before regeneration (corresponding to experiment in Table S9) using TEM (A), physisorption (B-D), and H_2 chemisorption (E). The total pore volume was 0.56 cm^3/g and the BET surface area is 678 m^2/g. The nickel dispersion was 6%.

Table S1. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 500 mg 5wt% Ni/C mixed with 3.0 g SiO_2 and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.1 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 0.6 h^{-1}.

		Total yield	Monomer yield/mol%								Oil yield
No.	Time/h	mol%	M1	M2	M3	M4	M5	M6	M7	other	wt%
1	4.0	20.6	2.9	-	-	17.7	-	-	-	-	-
2	6.1	43.6	6.4	-	-	37.3	-	-	-	-	85%
3	10.0	44.7	7.1	-	-	37.7	-	-	-	-	83%
4	22.2	44.6	7.2	-	-	37.5	-	-	-	-	85%
5	26.0	45.1	7.3	-	-	37.8	-	-	-	-	90%
6	30.0	44.4	7.1	-	-	37.3	-	-	-	-	84%
7	34.0	45.3	7.7	-	-	37.6	-	-	-	-	83%
8	47.3	45.0	7.2	-	-	37.7	-	-	-	-	82%
9	51.2	44.4	7.6	-	-	36.9	-	-	-	-	87%
10	55.0	44.8	7.3	-	-	37.6	-	-	-	-	83%
11	71.6	44.8	7.5	-	-	37.3	-	-	-	-	80%
12	80.0	44.2	7.1	-	-	37.1	-	-	-	-	78%
13	95.4	45.0	7.2	-	-	37.7	-	-	-	-	82%
14	105.6	44.0	7.2	-	-	36.9	-	-	-	-	81%
15	120.0	43.2	7.3	-	-	35.9	-	-	-	-	83%
16	125.7	43.6	7.3	-	-	36.3	-	-	-	-	76%

Table S2. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 500 mg 5wt% Ru/C mixed with 3.0 g SiO_2 and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.1 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 0.6 h^{-1}.

		Total yield	Monomer yield/mol%								Oil yield
No.	Time/h	mol%	M1	M2	M3	M4	M5	M6	M7	other	wt%
1	2.0	-	-	-	-	-	-	-	-	-	-
2	6.2	22.1	0.4	-	-	5.2	-	-	2.3	14.3	82%
3	10.0	28.8	0.7	-	-	8.1	-	-	7.8	12.1	87%
4	23.3	38.7	2.6	-	1.1	13.0	-	-	19.3	2.7	82%
5	27.0	38.4	3.4	-	1.1	16.3	-	-	17.0	0.6	88%
6	30.5	39.2	3.2	-	1.1	21.4	-	-	13.0	0.5	83%
7	34.8	39.0	3.7	-	-	24.0	-	-	10.8	0.5	84%
8	47.8	38.8	3.4	-	1.0	18.7	-	-	15.3	0.4	81%
9	51.8	38.2	3.7	-	-	21.0	-	-	13.1	0.4	85%
10	55.9	39.2	4.0	-	-	22.4	-	-	12.3	0.4	90%
11	57.9	38.5	3.9	-	-	20.5	-	-	13.6	0.5	84%
12	62.1	40.6	4.2	-	-	21.8	-	-	14.1	0.5	90%
13	66.1	38.8	3.6	-	-	22.5	-	-	12.3	0.5	85%
14	79.4	39.0	3.7	-	-	24.0	-	-	10.8	0.5	85%

Table S3. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 125 mg 5wt% Ni/C mixed with 3.6 g SiO_2 and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.1 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 2.4 h^{-1}. The catalyst was regenerated for the first time after sample No.14 and second time after sample No. 21.

		Total yield	Monomer yield/mol%								Oil yield
No.	Time/h	mol%	M1	M2	M3	M4	M5	M6	M7	other	wt%
1	2.1	24.2	3.6	-	-	20.6	-	-	-	-	-
2	6.0	37.5	5.7	-	-	31.8	-	-	-	-	84%
3	10.0	42.0	6.1	-	-	36.0	-	-	-	-	81%
4	24.0	39.7	5.4	-	-	34.3	-	-	-	-	92%
5	28.0	36.2	5.3	-	-	30.9	-	-	-	-	83%
6	31.0	36.6	5.4	-	-	31.1	-	-	-	-	80%
7	34.0	35.4	5.3	-	-	30.1	-	-	-	-	85%
8	48.1	32.6	4.9	-	-	27.6	-	-	-	-	86%
9	52.0	31.3	4.7	-	-	25.7	0.8	-	-	-	88%
10	55.0	30.0	4.4	-	-	24.7	0.9	-	-	-	86%
11	58.0	30.1	4.5	-	-	24.6	1.0	-	-	-	87%
12	72.4	28.0	4.3	-	-	22.3	1.5	-	-	-	80%
13	76.2	26.5	4.0	-	-	19.8	2.7	-	-	-	90%
14	81.1	24.6	3.9	-	-	18.3	2.5	-	-	-	90%
15	83.5	36.4	5.7	-	-	30.7	0.0	-	-	-	-
16	87.2	41.7	6.4	-	-	35.3	0.0	-	-	-	76%
17	91.2	38.5	5.2	-	-	31.0	2.2	-	-	-	82%
18	105.1	35.4	4.1	1.2	-	20.9	8.1	1.0	-	-	86%
19	114.8	32.6	2.8	1.6	-	14.0	12.5	1.7	-	-	84%
20	129.1	27.1	2.4	1.6	-	9.8	11.9	1.5	-	-	85%
21	131.5	25.6	2.3	1.8	-	8.1	11.8	1.6	-	-	90%
22	134.8	39.2	6.8	-	-	31.0	1.4	-	-	-	-
23	137.8	37.9	5.4	-	-	30.0	2.5	-	-	-	85%
24	140.5	35.2	4.8	1.0	-	24.9	4.5	-	-	-	84%
25	154.5	31.8	3.2	1.5	-	15.7	9.8	1.4	-	-	95%
26	157.8	29.5	2.4	1.9	-	11.0	12.4	1.9	-	-	83%
27	160.6	29.0	2.1	1.8	-	10.0	13.2	2.0	-	-	85%
28	163.7	28.4	2.3	2.0	-	9.5	12.6	2.0	-	-	86%
29	178.8	25.8	1.8	1.9	-	7.6	12.6	2.0	-	-	91%

Table S4. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 125 mg 5wt% Ru/C mixed with 3.6 g SiO_2 and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.1 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 2.4 h^{-1}. The catalyst was regenerated for the first time after sample No.14 and second time after sample No. 26.

		Total yield	Monomer yield/mol%								Oil yield
No.	Time/h	mol%	M1	M2	M3	M4	M5	M6	M7	other	wt%
1	2.0	14.0	0.5	-	-	3.7	-	-	6.9	0	-
2	6.0	37.0	1.8	-	2.4	8.5	-	-	21.5	3.0	88%
3	10.0	40.4	2.7	-	3.3	11.6	-	-	22.8	2.9	83%
4	24.7	42.7	3.6	-	2.6	16.6	-	-	19.9	-	85%
5	28.0	43.0	4.1	-	1.9	19.8	-	-	17.1	-	87%
6	31.0	43.0	4.2	-	1.5	21.0	-	-	16.2	-	85%
7	34.0	41.1	4.2	-	1.4	21.1	-	-	14.5	-	85%
8	48.0	40.4	4.2	-	1.2	21.7	1.9	-	11.5	-	80%
9	52.0	39.2	4.4	-	0.9	21.7	2.1	-	10.1	-	93%
10	55.0	35.7	4.2	-	-	21.5	1.2	-	8.8	-	86%
11	59.8	33.0	4.0	-	-	20.9	0.9	-	7.2	-	90%
12	73.1	30.6	3.8	-	-	18.7	2.0	-	6.0	-	87%
13	77.2	28.9	3.7	-	-	17.5	3.0	-	4.7	-	77%
14	81.1	26.5	3.5	-	-	15.9	2.9	-	4.1	-	90%
15	83.1	36.9	4.8	-	-	26.3	-	-	5.8	-	-
16	87.1	41.2	5.2	-	-	27.8	-	-	8.2	-	83%
17	91.1	40.9	5.0	-	-	27.0	-	-	8.9	-	79%
18	105.1	38.8	4.8	-	-	26.1	-	-	8.0	-	83%
19	109.1	38.6	4.6	-	-	27.4	-	-	6.7	-	84%
20	112.5	38.5	4.8	-	-	27.2	-	-	6.6	-	84%
21	115.6	37.9	4.9	-	-	26.6	-	-	6.4	-	82%
22	129.1	32.8	4.2	-	-	22.6	1.0	-	5.0	-	90%
23	133.2	29.8	4.1	-	-	20.4	1.4	-	3.8	-	96%
24	136.1	28.0	3.8	-	-	18.9	1.9	-	3.5	-	82%
25	139.1	26.4	3.7	-	-	17.7	1.8	-	3.2	-	84%
26	153.1	21.6	3.1	-	-	14.4	1.8	-	2.3	-	85%
27	155.2	34.4	4.8	-	-	25.1	-	-	4.6	-	-
28	158.3	40.0	5.3	-	-	27.8	-	-	6.8	-	72%
29	161.1	39.9	5.2	-	-	26.8	-	-	7.9	-	85%
30	175.1	37.9	5.0	-	-	25.4	-	-	7.5	-	86%
31	179.2	30.7	3.9	-	-	21.9	-	-	4.9	-	85%
32	182.1	29.7	4.0	-	-	20.9	-	-	4.8	-	83%
33	185.1	28.1	4.0	-	-	19.7	-	-	4.4	-	83%
34	199.1	24.6	3.6	-	-	16.2	1.6	-	3.2	-	90%
35	203.4	20.5	3.0	-	-	12.9	2.1	-	2.5	-	89%
36	206.3	19.8	3.0	-	-	12.3	2.4	-	2.2	-	85%

Table S5. Monophenolic monomer yield and oil yield resulting from the hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of only 3.8 g of SiO_2 without any metal catalyst and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.2 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar.

No.	Time/h	Total yield mol%	Monomer yield/mol%				Oil yield wt%
			Propenyl-guiaicol	Sinapyl alcohol	Propenyl-syringol (*E*)	Propenyl-syringol (*Z*)	
1	0.7	1.9	0.1	0.7	0.5	0.6	-
2	1.7	3.5	0.3	1.4	0.9	0.9	-
3	2.7	4.4	0.4	2.0	1.0	1.0	-
4	3.5	4.3	0.5	2.0	0.9	0.9	-
5	5.0	4.5	0.5	2.1	1.0	0.9	-

Table S6. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 150 mg 5wt% Ni/C mixed with 3.5 g SiO_2 and was held at 180 °C. The feed solution was 5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.2 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 8 h^{-1}.

No.	Time/h	Total yield mol%	Monomer yield/mol%								Oil yield wt%
			M1	M2	M3	M4	M5	M6	M7	other	
1	1.1	22.8	3.2	-	-	16.9	0.0	-	2.8	-	-
2	3.2	36.0	5.0	-	-	28.5	0.0	-	2.5	-	82%
3	4.1	36.5	5.4	-	-	28.8	0.0	-	2.2	-	80%
4	5.0	35.3	5.4	-	-	27.9	0.0	-	2.0	-	87%
5	7.2	31.7	5.0	-	-	25.2	0.6	-	0.9	-	90%
6	8.1	24.3	4.0	-	-	17.1	1.3	-	1.8	-	89%
7	10.1	24.7	4.0	-	-	16.9	2.4	-	1.4	-	93%
8	12.1	24.0	3.9	-	-	15.9	0.8	-	3.4	-	91%
9	14.1	22.1	3.6	-	-	13.7	4.3	-	0.5	-	92%
10	16.1	19.7	3.1	-	-	11.4	4.6	-	0.6	-	85%
11	17.1	14.2	1.9	-	-	7.2	4.3	-	0.0	-	88%
12	19.0	16.2	2.0	-	-	7.2	5.9	-	0.0	-	87%
13	21.1	16.6	2.2	-	-	6.2	7.1	-	0.0	-	90%
14	23.1	14.7	1.9	-	-	4.9	6.6	-	0.0	-	80%

Table S7. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 50 mg 5wt% Ni/C mixed with 3.7 g SiO_2 and was held at 180 °C. The feed solution was 5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.3 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 36 h^{-1}.

No.	Time/h	Total yield mol%	Monomer yield/mol%								Oil yield wt%
			M1	M2	M3	M4	M5	M6	M7	other	
1	0.8	20.0	2.6	-	-	16.2	1.1	-	-	-	-
2	1.9	19.6	2.5	-	-	11.2	5.5	-	-	-	-
3	3.0	14.7	1.8	-	-	5.9	6.2	-	-	-	-
4	4.0	11.1	1.3	-	-	3.7	5.3	-	-	-	-
5	5.2	8.7	0.8	-	-	2.4	4.6	-	-	-	-
6	6.1	7.30	0.7	-	-	1.7	4.0	-	-	-	-
7	7.0	6.2	0.5	-	-	1.2	3.6	-	-	-	-

Table S8. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 50 mg 5wt% Ni/C mixed with 3.7 g SiO_2 and was held at 180 °C. The feed solution was 5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.4 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 48 h^{-1}.

		Total yield	Monomer yield/mol%								Oil yield
No.	Time/h	mol%	M1	M2	M3	M4	M5	M6	M7	other	wt%
1	0.5	17.3	2.4	-	-	10.6	0.5	-	3.8	-	-
2	1.0	14.1	2.1	-	-	8.2	0.8	-	3.0	-	-
3	1.5	12.4	1.9	-	-	7.0	1.3	-	1.6	-	-
4	2.0	10.7	1.7	-	-	5.7	1.8	-	0.6	-	-

Table S9. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 125 mg of 5wt% Ni/C mixed with 3.6 g SiO_2 and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.1 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 2.4 h^{-1}.

		Total yield	Monomer yield/mol%								Oil yield
No.	Time/h	mol%	M1	M2	M3	M4	M5	M6	M7	other	wt%
1	2.0	24.2	3.2	-	-	21.0	-	-	-	-	-
2	6.0	39.3	5.5	-	-	33.8	-	-	-	-	-
3	9.0	41.4	5.9	-	-	35.5	-	-	-	-	-
4	23.0	39.0	5.6	-	-	33.4	-	-	-	-	-
5	27.0	38.6	5.7	-	-	32.9	-	-	-	-	-
6	30.0	37.9	5.5	-	-	32.4	-	-	-	-	-
7	33.0	36.6	5.3	-	-	31.2	-	-	-	-	-
8	47.0	36.1	5.3	-	-	30.8	-	-	-	-	-
9	51.0	35.1	4.8	-	-	30.2	-	-	-	-	-
10	54.0	34.1	4.9	-	-	28.5	0.8	-	-	-	-
11	57.0	30.0	4.6	-	-	24.3	1.1	-	-	-	-
12	71.0	27.7	4.1	-	-	22.2	1.4	-	-	-	-
13	75.0	26.2	4.5	-	-	19.8	1.9	-	-	-	-
14	79.5	23.8	4.9	-	-	16.5	2.4	-	-	-	-
15	82.0	21.7	3.2	-	-	15.5	2.9	-	-	-	-

Table S10. Monophenolic monomer yield and oil yield resulting from hydrogenolysis of propylidene acetal-stabilized lignin in flow. The catalyst bed consisted of 500 mg of 5 wt% Ni/SiO_2-Al_2O_3, 5 wt% Ni/TiO_2, or Ni/SiO_2 mixed with 3.0 g SiO_2 and was held at 180 °C. The feed solution was 2.5 mg/mL stabilized lignin in dioxane/methanol (2:8, v/v), which was introduced into the reactor at a flowrate of 0.1 mL/min by an HPLC pump. The flow rate of H_2 was 50 mL/min at a 60 bar. The WSHV was 0.6 h^{-1}.

No.	Time/h	Total yield mol%	Monomer yield/mol% M1	M2	M3	M4	M5	M6	M7	other	Oil yield wt%
Using Ni/SiO_2-Al_2O_3 as catalyst											
1	2.0	1.4	-	-	-	0.9	-	-	-	0.6	-
2	6.0	3.2	-	-	-	1.7	-	-	1.0	0.5	-
3	9.1	5.1	0.3	-	-	3.1	-	-	1.2	0.5	-
4	22.9	4.9	0.4	-	-	3.3	-	-	0.7	0.5	-
5	26.0	11.2	1.0	-	-	7.0	-	-	2.7	0.5	-
6	29.6	11.9	1.0	-	-	6.4	-	-	4.5	-	-
7	33.5	12.1	1.0	-	-	5.6	-	-	5.6	-	-
8	47.0	12.7	0.8	-	-	4.6	-	-	7.3	-	-
9	50.5	17.3	1.7	-	-	9.8	-	-	5.9	-	-
10	54.0	17.3	1.8	-	-	9.9	-	-	5.7	-	-
Using Ni/TiO_2 as catalyst											
1	2.0	-	-	-	-	-	-	-	-	-	-
2	5.8	0.5	-	-	-	-	-	-	-	0.5	-
3	9.0	4.8	-	-	-	-	-	-	3.4	1.4	-
4	23.4	6.7	-	-	-	-	-	-	4.7	2.0	-
5	26.3	6.3	-	-	-	-	-	-	4.5	1.8	-
6	27.3	6.2	-	-	-	-	-	-	4.5	1.8	-
Using Ni/SiO_2 as catalyst											
1	2.0	4.0	-	-	-	0.6	-	-	3.4	-	-
2	6.0	7.8	0.3	-	-	0.7	-	-	6.7	-	-
3	10.1	8.0	0.3	-	-	0.7	-	-	5.9	1.0	-
4	14.0	8.1	0.3	-	-	0.7	-	-	6.1	1.0	-

Table S11. Hydrogenolysis of acetal stabilized lignin with different catalysts in methanol and THF. Typically, 200 mg of propylidene acetal-stabilized lignin and 100 mg of solid catalyst were added into a parr reactor with 20 mL of methanol or THF. The reactions were performed under 200 °C with 40 bar of H_2 for 15 h.

			Monomer yield/mol %								
No.	Solvent	Catalyst	Total	M1	M2	M3	M4	M5	M6	M7	Other
1	MeOH	Ni/SiO_2-Al_2O_3	23.4	2.0	-	-	15.5	-	-	-	5.9
2	MeOH	Ni/TiO_2	33.3	2.5	-	1.7	15.1	-	-	11.5	2.56
3	MeOH	Ni/SiO_2	24.8	1.6	-	0.8	10.9	-	-	4.0	7.5
4	MeOH	Active carbon	22.4	3.2	0.2	-	16.6	0.3	-	-	2.1
5	MeOH	SiO_2-Al_2O_3	13.8	1.2	0.5	-	6.1	4.1	-	-	1.9
6	MeOH	TiO_2	17.2	1.0	0.2	-	7.8	2.0	-	-	6.2
7	MeOH	SiO_2	14.6	0.6	0.9	-	3.4	6.8	-	-	2.9
8	THF	SiO_2-Al_2O_3	3.3	0.2	-	-	2.0	1.1	-	-	-
9	THF	Active carbon	7.4	0.3	1.1	-	1.0	5.0	-	-	-
10	MeOH	No catalyst	13.2	0.6	0.7	-	3.5	5.5	-	-	2.9
11	THF	No catalyst	-	-	-	-	-	-	-	-	-

Table S12. Physisorption and dispersion of the metal oxide catalysts.

	BET surface area (m^2/g) [a]	Pore volume (cm^3/g) [a]	Metal dispersion [b]
Ni/TiO_2	54	0.41	4%
Ni/SiO_2	53	0.37	5%
Ni/SiO_2-Al_2O_3	295	0.94	10%

[a] BET surface area and pore volume were determined by N_2 physisorption.

[b] Metal dispersion was determined by the quantity of surface metal (determined by particle size distribution from TEM images) over the amount of total metal present.

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