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Supplementary Information

Selective depolymerization of lignin catalyzed by nickel supported on zirconium phosphate

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Materials

The organosolv lignin was separated from local sugarcane bagasse according to the reported procedure [1]. NREL method shows that the total residual sugar content is 3.53 wt%. Tetrahydrofuran (THF, HPLC grade) and d_6-DMSO were provide by J & K Chemical Reagent Co., Ltd. (Beijing, China). Methanol, ethanol and isopropanol were supplied by Tianjin chemical reagent factory (Tianjin, China). $NH_4H_2PO_4$ and $ZrOCl_2 \cdot 8H_2O$ were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Other reagents were supplied by Jinhuada Chemical Reagent Co., Ltd. (Guangzhou, China). All reagents are of analytical grade and were used without further purification.

Catalyst synthesis

The zirconium phosphate supporters (ZrP-X, where X stands for the different molar ratio of P to Zr) were synthesized according to the deposition precipitation method [2]. Taking the synthesis of ZrP-2.0 as the example, a typical procedure was carried out as follows. 280 mL $NH_4H_2PO_4$ solution (0.5 mol L^{-1}) was added rapidly into 70 ml $ZrOCl_2 \cdot 8H_2O$ solution (1.0 mol L^{-1}) in a three-necked flask under continuous stirring at room temperature. Then the obtained white precipitate was filtered, washed with deionized water (250 mL×3) and dried at 100 °C for 24 h. After trituration to 80-120 mesh, the solid powder was calcined at 400 °C for 4 h to give the final ZrP-2.0 supporter. Other ZrP carriers were prepared following the similar procedure as ZrP-2.0 with various $NH_4H_2PO_4$ concentrations.

The catalyst of Ni/ZrP-X was prepared by wetness impregnation method.

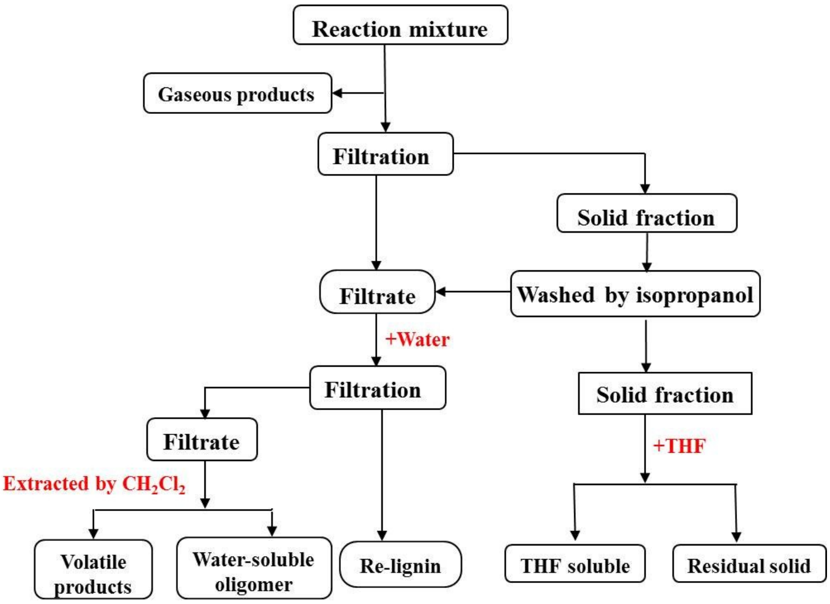
Appropriate amounts of as synthesized ZrP-X supporter (1.0 g) was impregnated with $Ni(NO_3)_2 \cdot 6H_2O$ solution containing a quantitative Ni to achieve the theoretical Ni loading. The impregnated sample was then remained in air for 12 h at room temperature followed by drying at 120 °C for 2 h. Finally, the obtained light green powder was calcined at 550 °C for 4 h and reduced at 550 °C for another 4 h in a flow of reducing gas (100% H_2) prior to use. The elemental compositions and the crystal structure of the synthesized samples were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray powder diffraction (XRD) respectively.

Typical process for lignin hydrogenolysis

All lignin depolymerization reactions were carried out in a 100 mL stainless autoclave equipped with a mechanical agitation. For a typical procedure, 0.5 g bagasse lignin, 0.10 g Ni-based catalyst and 20 mL isopropanol were added into the autoclave in sequence. Then the reactor was sealed, displaced by hydrogen for three times and pressurized to 2.0 MPa. After that, it was heated to designated temperature (240-280 ˚C) and maintained for desired time (1-5 h) under the stirring of 650 rpm. When the designated time was elapsed, the autoclave was cooled down to room temperature using flowing water. Triplicate experiments were conducted for the standard error reduction.

Product separation and analysis

Typical procedure for lignin depolymerization product separation was shown in Scheme S1. The gaseous products were collected in an air-bag. The solid fraction was first separated from the mixture by filtration, and then, it was washed using isopropanol (5 mL × 3) and THF (5 mL × 3) respectively. The residual solid (including catalyst and THF insoluble product) was dried at 120 ˚C until constant weight. The THF soluble fraction was first submitted for solvent removal, and then, it was dried under vacuum at 80 ˚C until constant weight, the finally obtained viscous liquids was denoted as phenolic oligomer. The filtrate and the isopropanol which was used for solid washing were first collected and then added by 150 mL deionized water to precipitate the incompletely reacted lignin. After aging at room temperature for 12 h, the precipitate was isolated and dried under vacuum at 80 ˚C for 12 h, giving a brown solid which was designated as regenerated lignin (Re-lignin). The volatile chemicals in the liquid fraction were extracted using 30 mL dichloromethane (CH_2Cl_2) for three times (10 mL × 3). The organic phase was then diluted to 50 mL in a volumetric flask using fresh CH_2Cl_2.



Scheme S1. Typical procedure for lignin depolymerization product separation

The gaseous fraction from this process was identified by gas chromatography (Agilent 7890B) with a thermal conductivity detector (GC-TCD) using an extra-standard method. The volatile products (CH_2Cl_2 soluble fraction) were qualitatively and quantitatively analyzed on an Agilent gas chromatography equipped with both mass and flamed ionization detectors (GC-MS-FID, Agilent 7890B/5977). The chemicals were separated on a HP-INNOWAX column (30 m × 0.25 mm × 0.25 μm) and identified according to the Agilent NIST MS library. The FID was operated at 270 ˚C with 1.0 mL min^{-1} helium as the carrier gas. The initial oven temperature was 50 ˚C (held for 3 min), and then it was ramped to 250 ˚C (held for another 1 min) with the speed of 10 ˚C min^{-1}.

Characterization of original and regenerated lignin and phenolic oligomer

The Fourier transform infrared spectroscopy (FT-IR) spectra were obtained from a Bruker Tensor 27 FT-IR spectrophotometer in the range of 400-4000 cm^{-1}. Elemental analysis was conducted on a Vario EL III elementary analyzer, where the oxygen content was calculated according to the mass conservation based upon the assumption that the samples only contain of C, H, N, S and O. The average molecular weight of raw lignin and Re-lignin were measured by gel permeation chromatography (GPC) on an Agilent 1260 high performance liquid chromatography (HPLC) with a refractive index detector (RID). THF (HPLC grade) was used as eluent at a flow rate of 1.0 mL min^{-1}. Polystyrene standards was employed for molecular weight calibration. Nuclear magnetic resonance (^1H NMR and ^{13}C-NMR) spectra of original lignin and Re-lignin were recorded at 25 °C on a Bruker AV-400 spectrometer. The heteronuclear single quantum correlation (HSQC) spectra were performed on a Bruker Avance III 600 MHz spectrometer. About 100 mg lignin was dissolved in 1.0 mL d_6-DMSO. The spectral widths were 5000/20000 Hz for ^{1}H/^{13}C-dimension, respectively. The number of collected complex points was 1024 for ^{1}H-dimension with a recycle delay of 1.5 s. Data processing was performed using standard Bruker Topspin-NMR software.

Table S1 Elemental compositions of different catalysts determined by ICP-AES

Samples	Ni (wt%)	P/Zr ratio	Ni (ppm)	P (ppm)	Zr (ppm)
ZrP-2.0	n. d.	1.87	n. d.	6.24	3.34
5%Ni/(ZrP-2.0)	5.02	1.91	0.88	6.16	3.23
10%Ni/(ZrP-2.0)	10.1	1.86	1.77	5.92	3.18
15%Ni/(ZrP-2.0)	14.6	1.88	2.90	6.20	3.29
20%Ni/(ZrP-2.0)	19.4	1.87	3.40	5.61	3.00
25%Ni/(ZrP-2.0)	22.6	1.89	3.96	5.40	2.94
15%Ni/(ZrP-1.0)	14.8	1.06	3.02	4.39	4.14
15%Ni/(ZrP-1.5)	15.1	1.57	3.09	5.38	3.42
15%Ni/(ZrP-2.5)	14.9	2.38	3.00	5.78	2.43
15%Ni/(ZrP-3.0)	14.7	3.03	3.13	6.75	2.23

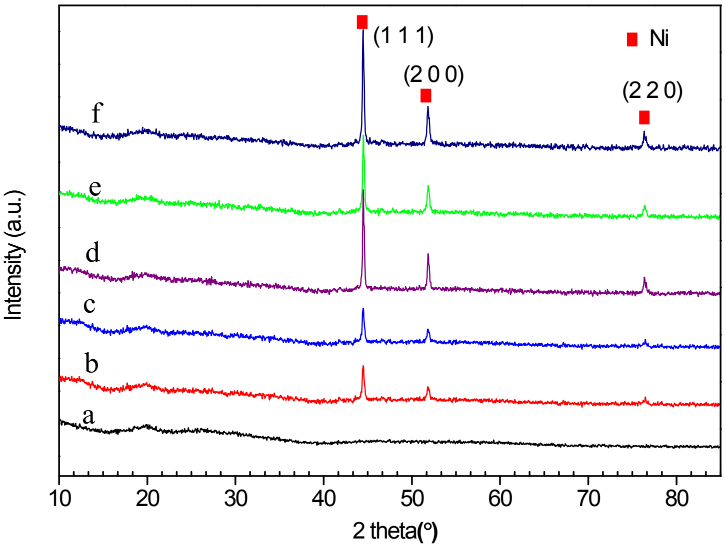


Figure S1 XRD patterns of Ni/ZrP-X samples

(a) ZrP-2.0; (b) 5% Ni/ ZrP-2.0; (c) 10% Ni/ ZrP-2.0; (d) 15% Ni/ ZrP-2.0; (e) 20% Ni/ ZrP-2.0; (f) 25%Ni/ ZrP-2.0

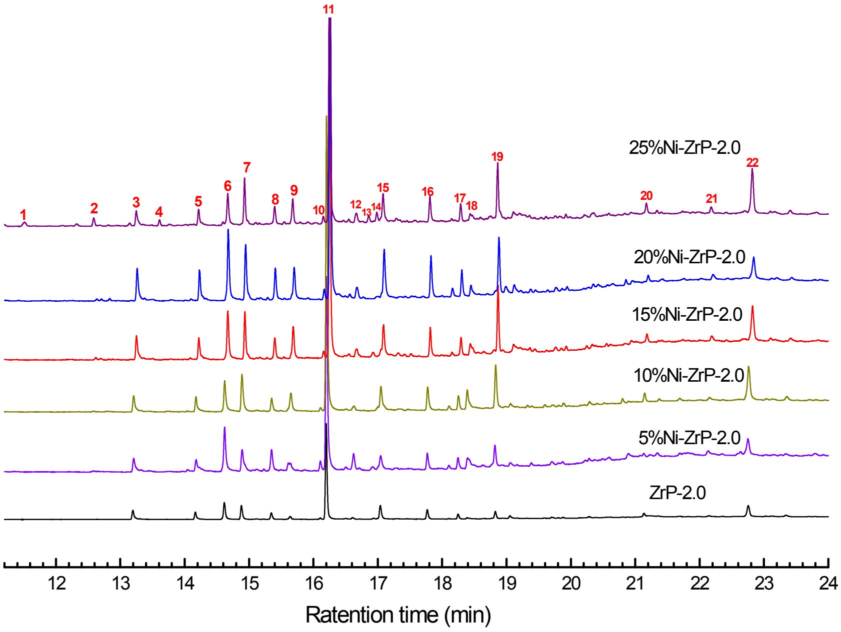


Figure S2 GC-MS profile of lignin conversion over ZrP-2.0 catalyst with different Ni loading

Table S2 The main components of the volatile depolymerization products

NO	RT (min)	Component	NO	RT (min)	Component
1	11.52	Heptadecane	12	16.66	Benzenemethanol,4-(1,1-dimethylethyl)-
2	12.59	Octadecane	13	16.84	i-Propyl hexadecanoate
3	13.23	Phenol, 2-methoxy-	14	16.98	Hexadecanoic acid, ethyl ester
4	13.61	Nonadecane	15	17.08	Phenol, 2,6-dimethoxy-
5	14.21	Phenol, 2-methoxy-4-methyl-	16	17.52	Benzoic acid
6	14.66	Phenol	17	17.80	Benzoic acid, 4-hydroxy-3-methoxy-
7	14.94	Phenol,4-ethyl-2-methoxy-	18	18.29	Benzene,1,2,3-trimethoxy-5-methyl-
8	15.40	Phenol, 4-methyl-	19	18.85	Benzeneacetaldehyde, .alpha.-phenyl-
9	15.69	Phenol, 2-methoxy-4-propyl-	20	21.02	beta.-(4-Hydroxy-3-methoxyphenyl)propionic acid
10	16.10	Phenol, 2-(1-methylethyl)-	21	22.21	Octaethylene glycol monododecyl ether
11	16.24	Phenol, 4-ethyl-	22	22.79	Benzenepropanoic acid, 4-hydroxy-

Conditions: organosolv bagasse lignin 0.5 g, catalyst 0.10 g, isopropanol 20 mL, H_2 2.0 MPa, 270 °C, 4 h.

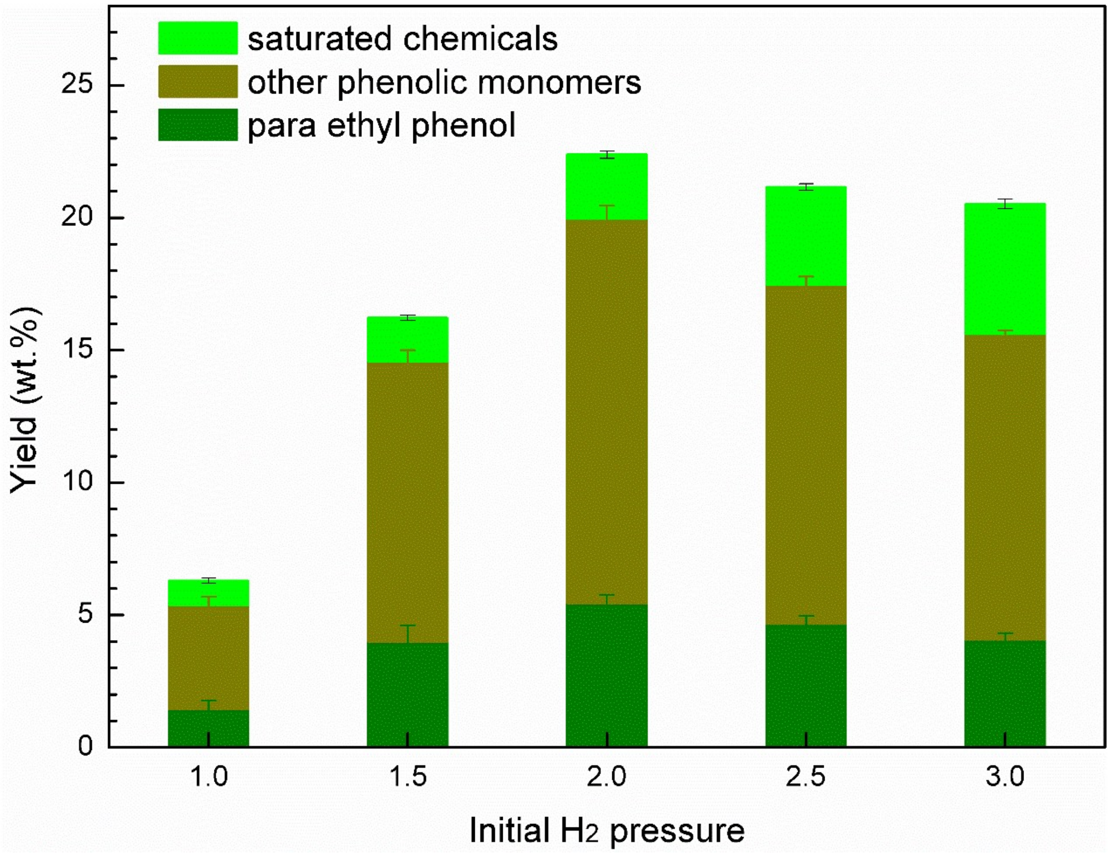


Figure S3 Product distribution of the volatile fraction

Note: the saturated chemical is designated as the compounds which can be identified by GC-MS, including *para* ethyl cyclohexane, *para* ethyl cyclohexanol and others without benzene ring. It is noteworthy that this compound composition is good agreement with that of the reported work [3].

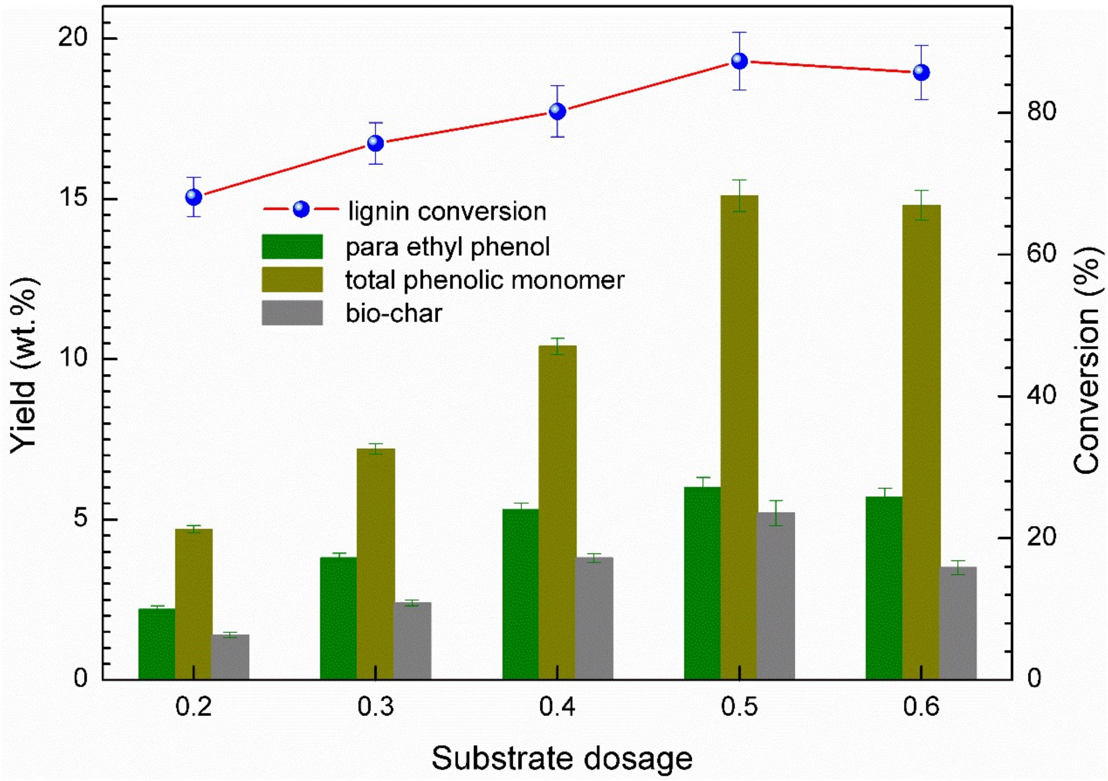


Figure S4 The effect of substrate amount on the lignin hydrogenolysis

Condition: 15%Ni/ZrP-2.0 catalyst 0.10 g, isopropanol 20 mL; H_2 2.0 MPa, 260 °C, 4 h.

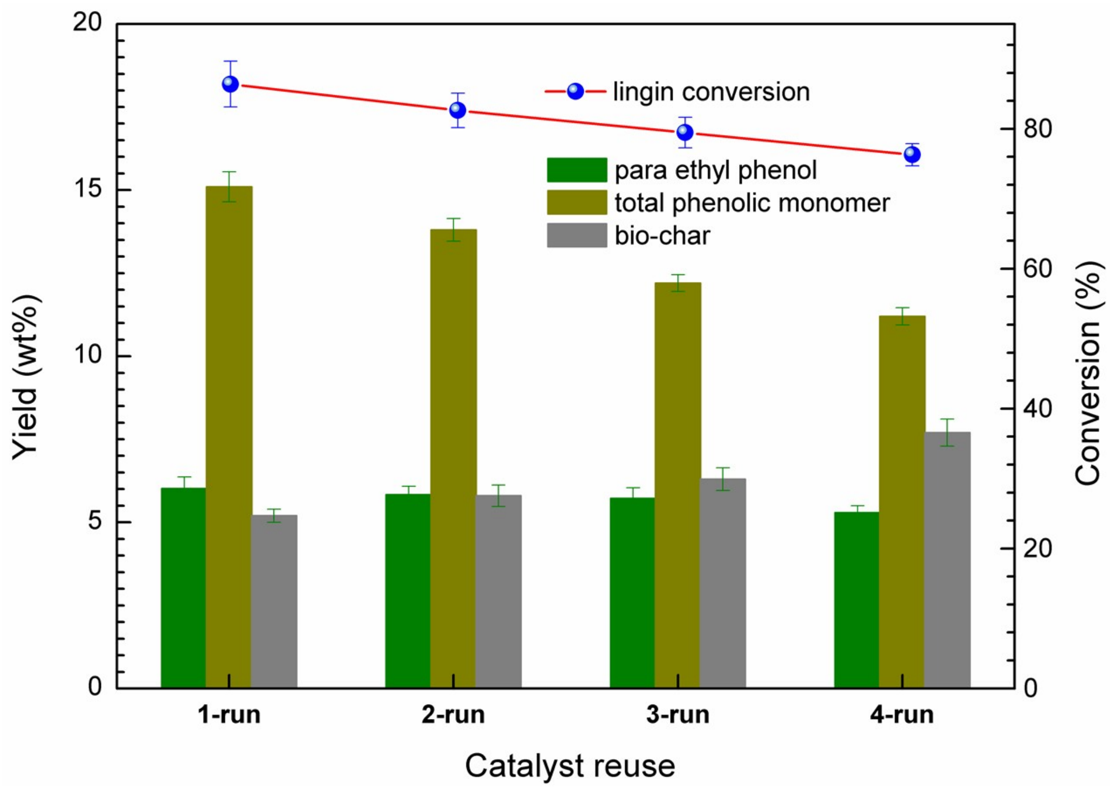


Figure S5 The recyclability of 15%Ni/ZrP-2.0

Conditions: organosolv lignin 0.50 g, isopropanol 20 mL; H_2 2.0 MPa, 260 °C, 4 h.

Table S3 The main components of volatile products from the optimized condition. [a]

RT (min)	Component	Yield (wt%)[b]		RT (min)	Component	Yield (wt%)[b]
	Phenols	8.53			**Syringols**	0.85
14.66	Phenol	0.59		17.08	Phenol, 2,6-dimethoxy-	0.75
15.40	Phenol, 4-methyl-	0.23		19.09	1,2-Benzenediol, 3-methoxy-	0.10
16.24	Phenol, 4-ethyl-	6.05				
22.79	Benzenepropanoic acid, 4-hydroxy-	1.61			**Others**	3.04
13.75	Butylated hydroxytoluene	0.05		16.66	o-Isopropylphenetole	0.23
	Guaiacols	2.71		17.52	Benzoic acid	0.53
13.23	2-methoxy-Phenol	0.47		18.29	Benzene,1,2,3-trimethoxy-5-methyl-	0.28
14.21	Phenol, 2-methoxy-4-methyl-	0.38		18.85	Benzeneacetaldehyde, alpha.-phenyl-	1.14
17.80	Benzoic acid, 4-hydroxy-3-methoxy-	0.45		21.02	Beta-(4-hydroxy-3-methoxyphenyl)propionic acid,	0.31
14.94	Phenol, 4-ethyl-2-methoxy-	0.91				
15.69	Phenol, 2-methoxy-4-propyl-	0.50				

[a] Conditions: organosolv bagasse lignin 0.5 g, 15%Ni/ZrP-2.0 catalyst 0.10 g, isopropanol 20 mL; H_2 2.0 MPa, 260 °C, 4 h.

[b] The yields of volatile products were measured by internal standard method using *n*-octanol as standard compound, the calibration factor was calculated according to *para* ethyl phenol, *para* ethyl guaiacol and syringol respectively.

Table S4 Assignment of main lignin ^{13}C-^{1}H cross-signals in the HSQC spectra

Label	δ_C/δ_H (ppm)	Assignment
C_β	53.2/3.76	C_β–H_β in phenylcoumarane substructures (C)
B_β	53.8/3.86	C_β–H_β in resinol substructures (B)
$-OCH_3$	56.1/3.77	C–H in methoxyls
A_γ	59.3~61.3/3.57~3.76	C_γ–H_γ in β-O-4′ substructures (A)
C_γ	71.2/3.75	C_γ–H_γ in phenylcoumaran substructures (C)
B_γ	65.1/3.66	C_γ–H_γ in resinol substructures (B)
A_α	72.7/4.85	C_α –H_α in β-O-4′ substructures (A)
A_β	80.9/4.53	C_β –H_β in β-O-4′ substructures linked to G and H units (A)
B_α	86.1/5.47	C_α –H_α in resinol substructures (B)
$S_{2,6}$	105.6/6.72	$C_{2,6}$–$H_{2,6}$ in etherified syringyl units (S)
$S'_{2,6}$	106.1/7.54	$C_{2,6}$–$H_{2,6}$ in oxidized (C_α=O) syringyl units (S′)
G_2	112.7/7.06	C_2–H_2 in guaiacyl units (G)
G_5	115.8/6.91	C_5–H_5 in guaiacyl units (G)
G_6	122.5/6.72	C_6–H_6 in guaiacyl units (G)
$H_{2,6}$	128.2/7.31	$C_{2,6}$–$H_{2,6}$ in p-hydroxyphenyl units (H)
$PB_{2,6}$	133.9/7.62	$C_{2,6}$–$H_{2,6}$ in free p-hydroxybenzonic acid (PB)
$PCA_{2/6}$	130.9/7.46	$C_{2,6}$–$H_{2,6}$ in p-coumarate (*p*CA)
$PCA_{3/5}$	117.2/6.74	$C_{3,5}$–$H_{3,5}$ in p-coumarate (*p*CA)
PCA_7	145.4/7.55	C_7–H_7 in *p*-coumarate (*p*CA)
PCA_8	115.1/6.31	C_8–H_8 in p-coumarate (*p*CA)
FA_2	112.5/7.31	C_2–H_2 in ferulate (FA)
FA_7	145.5/7.33	C_7–H_7 in ferulate (FA)
FA_8	116.3/6.57	C_8–H_8 in ferulate (FA)

FT-IR spectra of the raw and regenerated lignin

The evolution of FT-IR spectra of raw and Re-lignin from the hydrogenolysis process over various catalysts are shown in Fig. S6. It has been reported that the peaks at 3450–3300, 2921, and 2852 cm^{-1} are responded for the stretching of -OH, -CH_2, and -OCH_3 group, respectively [4]. 1710 cm^{-1} is considered as the characteristic absorption of unconjugated carbonyl, while the peaks at 1600, 1507, 1453 and 837 cm^{-1} are assigned as the characteristic absorbance values of benzene structure of lignin [5]. The absorbance at 1328 and 1118 cm^{-1} corresponds to the syringyl ring breathing with C-O stretching and syringyl-type aromatic C-H in plane deformations, respectively [6]. The peaks at 1269 and 837 cm$^{−1}$ are considered to be the characteristic absorbance of guaiacyl units. The absorbance at 1213 cm$^{−1}$ relates to ring breathing of both syringyl and guaiacyl structure with C-O stretching[7]. Furthermore, the peak at 1176 cm$^{−1}$ represents the *p*-coumaryl unit in lignin, and the signal at 1034 cm$^{−1}$ indicates plane aromatic skeletal vibrations and primary hydroxyl group in *β*-hydroxy coniferyl alcohol [8]. These FT-IR spectra illustrate that the Re-lignins from various catalytic conditions show a typical lignin FT-IR absorption bands, where the benzene ring and other characteristic groups (for instance, methoxyl and phenol hydroxyl) can be observed clearly. It suggests the reservation of lignin “core” structure. Nevertheless, the thorough disappearance of FT-IR absorbance at 1176 cm^{-1} in the Re-lignin indicates clearly the ready conversion of *p*CA structure unit, which is responsible for the highly selective generation of *para* ethyl phenol. The significant strength weakening of the absorption band at 1034 cm^{-1} also suggests the conversion of $H_{2,6}$ structure of lignin. By contrast, the characteristic absorbance of G and S lignin are still remained because of the relatively slight degradation of these structural units. Additionally, a weakened peak strength at 1710 cm^{-1} is exhibited for the Re-lignin in comparison with that of benzene ring. It implies the cleavage of linkage between aromatic fraction and carbonyl group, yielding the carbonyl containing products (Table S2).

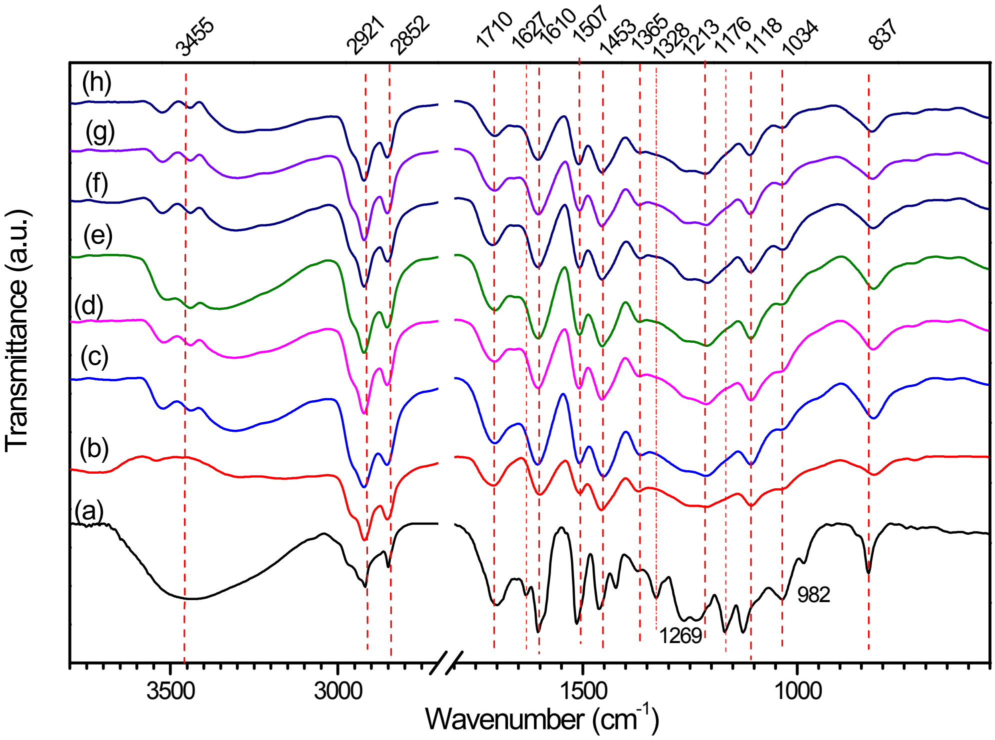


Figure S6 FT-IR spectra of raw lignin (a) and regenerated lignin with various catalysts: (b) None; (c)ZrP-2.0; (d) 5% Ni/ZrP-2.0; (e) 10% Ni/ZrP-2.0; (f) 15% Ni/ZrP-2.0; (g) 20% Ni/ZrP-2.0; (h) 25% Ni/ZrP-2.0.

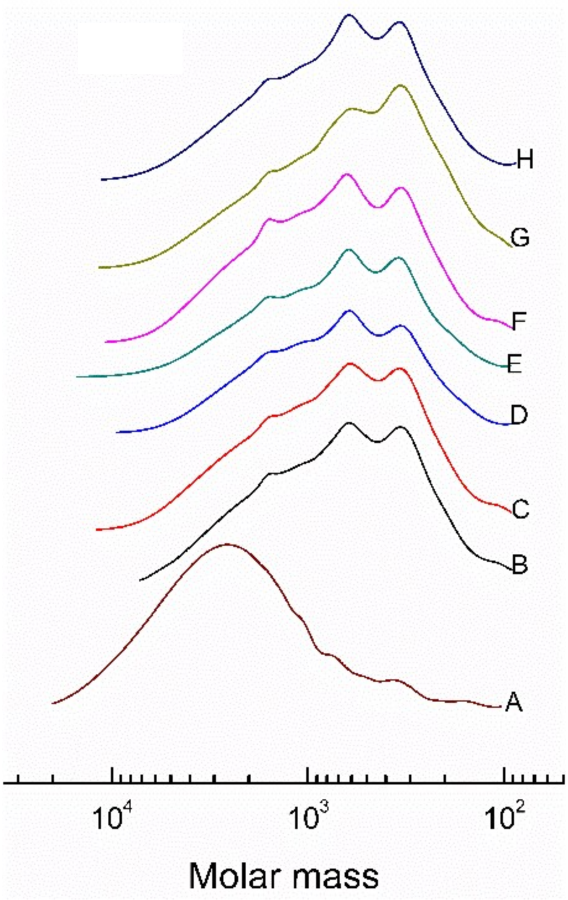


Figure S7 GPC analysis of the original lignin and Re-lignin

Sample (A) raw lignin; (B) no catalyst; (C) ZrP-2.0; (D) 5% Ni/ZrP-2.0; (E) 10% Ni/ZrP-2.0; (F) 15% Ni/ZrP-2.0; (G) 20%Ni/ZrP-2.0 and (H) 25% Ni/ZrP-2.0.

Table S5. Average molecular weight of raw and recovered lignin.

Materials [a]	Mn	Mw	Mz	D[b]
Raw lignin	920	2263	3494	2.46
Recovered lignin A	451	1129	2450	2.50
Recovered lignin B	512	1231	2501	2.40
Recovered lignin C	525	1268	2520	2.41
Recovered lignin D	529	1319	2679	2.49
Recovered lignin E	530	1195	2218	2.25
Recovered lignin F	519	1268	2682	2.44
Recovered lignin G	554	1294	2470	2.34
Recovered lignin H	534	1121	2363	2.08
oligomer L	219	411	739	1.88

[a] Recovered lignin from depolymerization process as listed in Table 1, (A) no catalyst; (B) ZrP-2.0; (C) 5% Ni/ZrP-2.0; (D) 10% Ni/ZrP-2.0; (E) 15% Ni/ZrP-2.0; (F) 20% Ni/ZrP-2.0; (G) 25% Ni/ZrP-2.0; (H) 15% Ni/ZrP-2.0 under optimized condition.

[b] Mn: number average molecular weight; Mw: weight average molecular weight; Mz: Z-average molecular weight; D: dispersion degree.

Table S6 Elemental analysis of the raw lignin, phenolic oligomer and regenerated lignin from different catalytic system [a]

Catalyst	Element content (wt%)					Molecular formula	HHV ($MJ\ kg^{-1}$)[c]
	C	H	O [b]	N	S		
Raw lignin	59.97	5.74	32.79	0.960	0.539	$C_9H_{10.33}O_{3.69}N_{0.12}S_{0.03}$	22.62
Blank	64.39	6.14	27.98	0.917	0.575	$C_9H_{10.28}O_{2.93}N_{0.11}S_{0.03}$	25.54
ZrP-2.0	67.43	6.31	24.74	1.079	0.437	$C_9H_{10.12}O_{2.48}N_{0.12}S_{0.02}$	27.39
5% Ni/ZrP-2.0	70.96	6.52	21.24	0.897	0.379	$C_9H_{9.92}O_{2.02}N_{0.10}S_{0.02}$	29.50
10% Ni/ZrP-2.0	71.92	6.62	20.20	0.922	0.342	$C_9H_{9.95}O_{1.90}N_{0.10}S_{0.02}$	30.16
15% Ni/ZrP-2.0	73.39	6.68	18.61	0.979	0.342	$C_9H_{9.82}O_{1.71}N_{0.10}S_{0.02}$	31.02
20% Ni/ZrP-2.0	74.79	6.75	17.14	0.970	0.344	$C_9H_{9.72}O_{1.55}N_{0.10}S_{0.02}$	31.86
25% Ni/ZrP-2.0	75.12	6.71	16.83	0.975	0.370	$C_9H_{9.64}O_{1.51}N_{0.10}S_{0.02}$	31.96
15% Ni/ZrP-2.0[d]	74.74	6.73	17.28	0.918	0.330	$C_9H_{9.70}O_{1.56}N_{0.10}S_{0.02}$	31.78
Oligomer	66.40	6.49	25.82	1.017	0.268	$C_9H_{10.55}O_{2.62}N_{0.12}S_{0.01}$	27.10

[a] The samples were dried at 120 °C until constant weight;

[b] The oxygen content was estimated by the conservation of mass based on the assumption that the samples only contain C, H, N, S and O;

[c] The HHV value was evaluated by Dulong Formula: HHV (MJ/kg) = 0.3383 × C + 1.422 × (H - O/8).

[d] The Re-lignin sample was gained under the optimized condition (260 °C, 4 h and 2.0 MPa H_2).

The detailed calculation procedure for lignin conversion to phenolic oligomer

- As exhibited in Fig. 6, 87.3 wt% of lignin is converted under the optimized conditions. Elemental analysis demonstrates that the carbon content of Re-lignin is 74.74% (Table S6). Therefore, the reserved carbon in the Re-lignin is (100%-87.3%) × 74.74% = 9.49%

The converted lignin carbon atom includes three parts, phenolic monomer, oligomer and bio-char. The yield of bio-char is already measured according to the carbon comparison. The carbon atom in the volatile product is measured according to their yields and molecular carbon contents respectively (Eq. 1). It is found to be 16.51%.

$$\text{Lignin conversion to volatile products} = \left(\sum_{i=1}^{n} m_{p_i} \times C_{p_i}\right) \Big/ m_L \times C_L \times 100\% \qquad \text{Eq.S1}$$

- Therefore, the lignin carbon which is converted to phenolic oligomer is the different between the original lignin and those for Re-lignin, bio-char and volatile products respectively. Namely, it is 59.97% - 9.49% - 5.2% - 16.51%=28.77%
- Finally, the conversion of lignin to phenolic oligomer is 28.77%/59.97% × 100% = 48%

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