Supporting information

Self-hydrogen Supplied Catalytic Fractionation of Raw Biomass into Lignin-derived Phenolic Monomers and Cellulose-rich Pulps

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Table of Contents

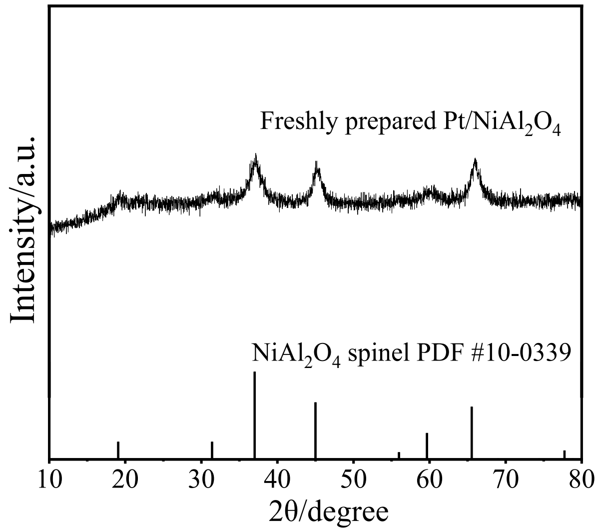


Figure S1. XRD patterns of the Pt/$NiAl_2O_4$ catalyst.

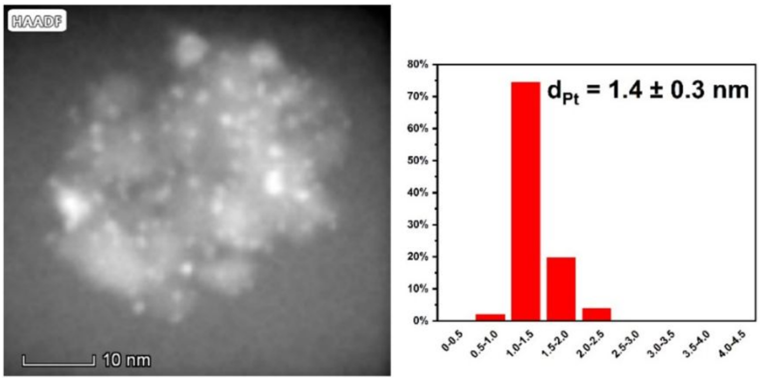


Figure S2. HAADF-STEM and Particle size distributions of Pt in the freshly prepared Pt/$NiAl_2O_4$ catalyst.

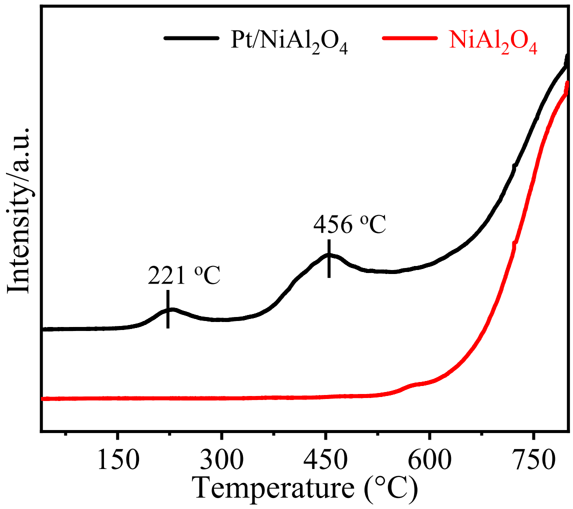


Figure S3. H_2-TPR profile of Pt/$NiAl_2O_4$ and $NiAl_2O_4$.

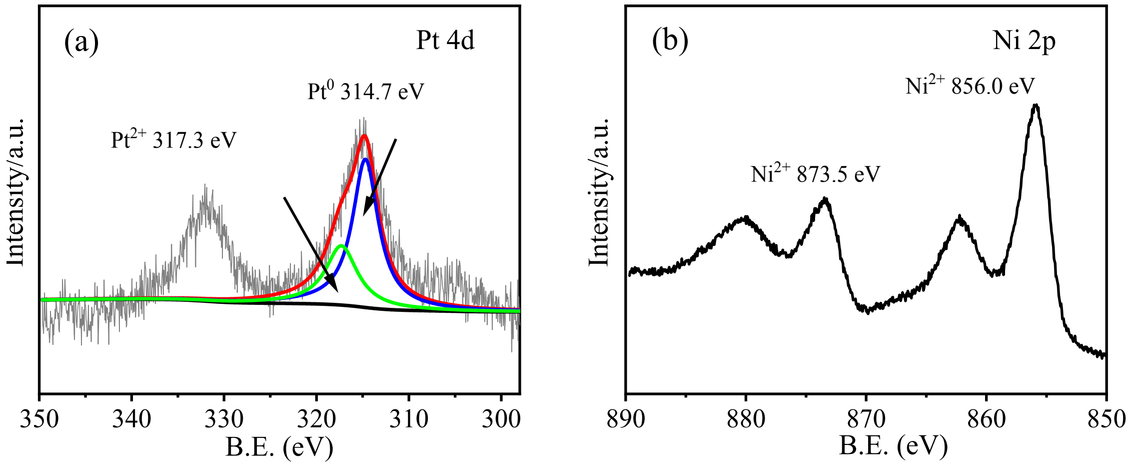


Figure S4. XPS spectra of (a) Pt 4d and (b) Ni 2p over the Pt/$NiAl_2O_4$ catalyst.

The X-ray diffraction (XRD) patterns exhibited typical peaks ascribed to $NiAl_2O_4$ (PDF # No. 10–0339), while there were no detectable Pt-related peaks, probably owing to the high dispersion of Pt and small particle size (Figure S1 & S2). The reduction peak at 221 ^{o}C in H_2-TPR profile (Figure S3) can be assigned to the reduction of PtOx and the peak at 456 ^{o}C is related to the co-reduction of PtOx and NiOx species.[1] The Pt $4d_{5/2}$ spectra in XPS spectra can be divided into two parts, 314.7 eV corresponding to the Pt^{0} species, and 317.3 eV to the Pt^{2+} species (Figure S4). While the chemical state of Ni is mainly composed of Ni^{2+} species, 873.5 eV and 856.0 eV.[2]

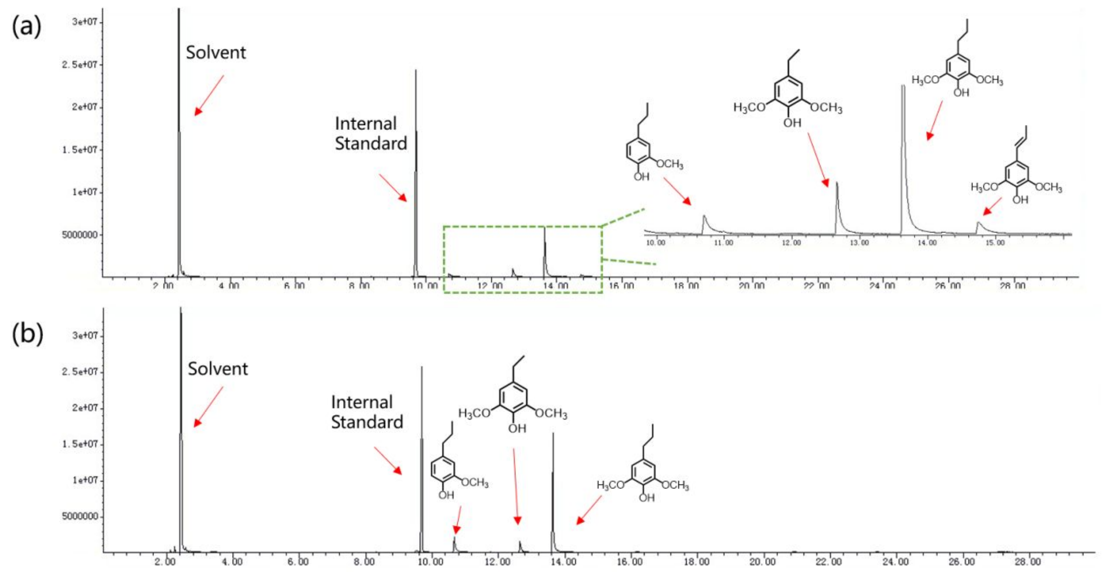
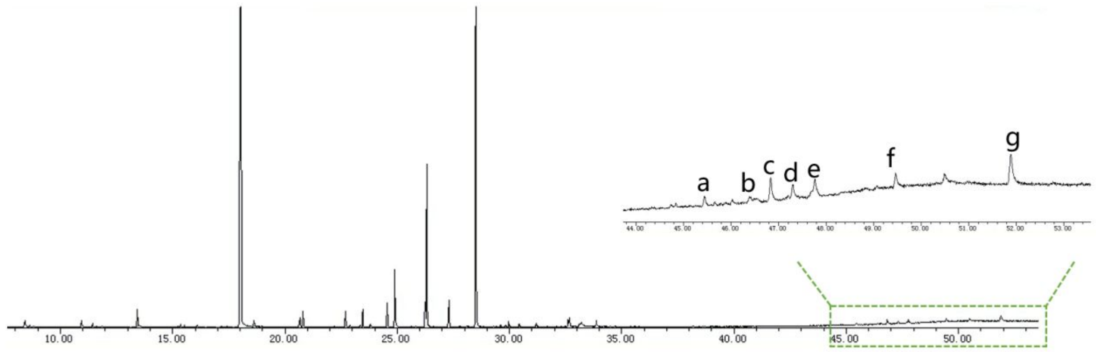
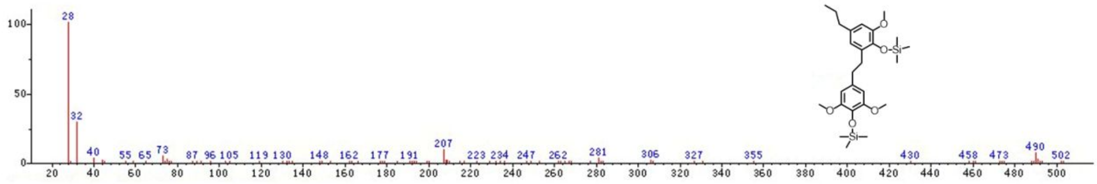


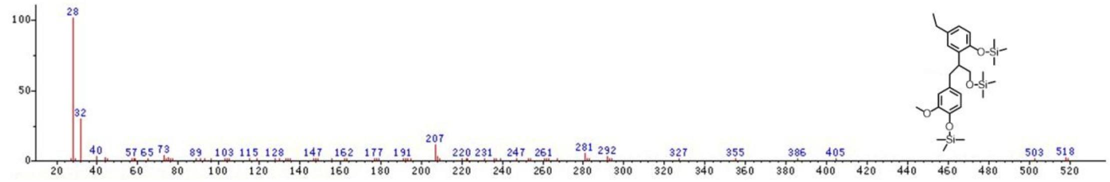
Figure S5. GC spectra of the lignin-derived monomers from birch over the Pt/$NiAl_2O_4$ catalyst. Reaction conditions: birch sawdust (0.5 g), Pt/$NiAl_2O_4$ (0.1 g), H_2O (10 mL), 140 °C, N_2 1 atm, 12 h for (a) and 24 h for (b).



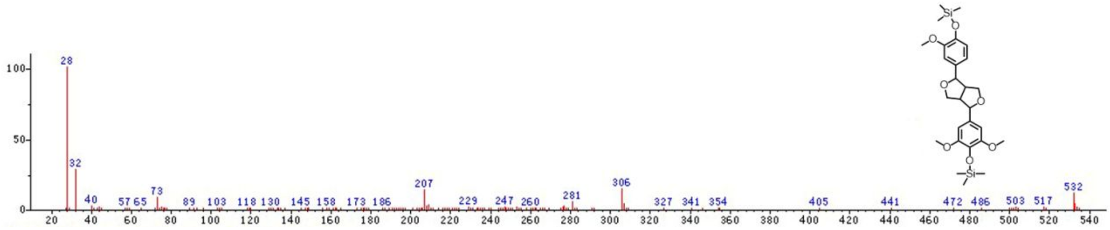
Dimer a (β-5): Molecular weight: 490



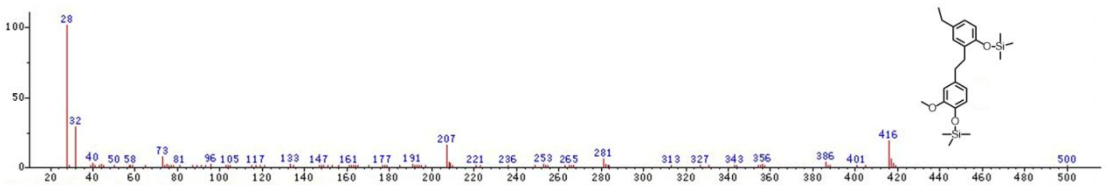
Dimer b (β-5): Molecular weight: 518



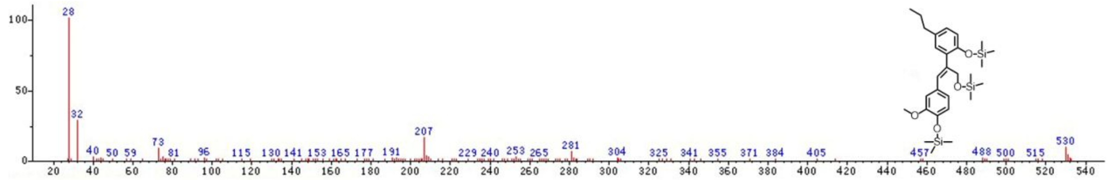
Dimer c (β-β): Molecular weight: 532



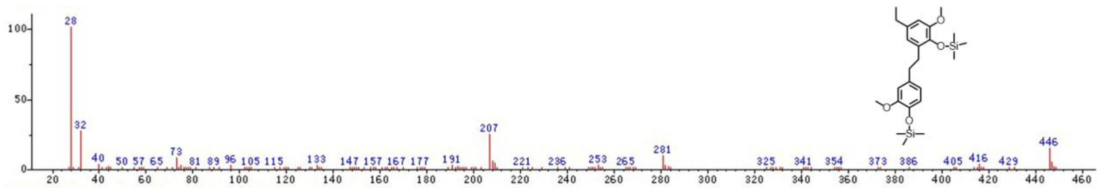
Dimer d (β-5): Molecular weight: 416



Dimer e (β-5): Molecular weight: 530



Dimer f (β-5): Molecular weight: 446



Dimer g (β-5): Molecular weight: 476

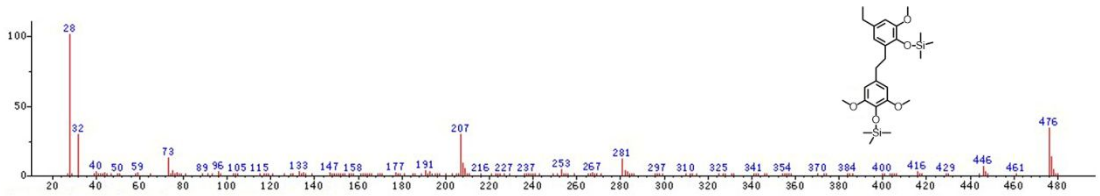


Figure S6. The information on the possible dimers of the lignin oils. (GC-MS spectra of silylated lignin oils and structure analyses for possible dimers).

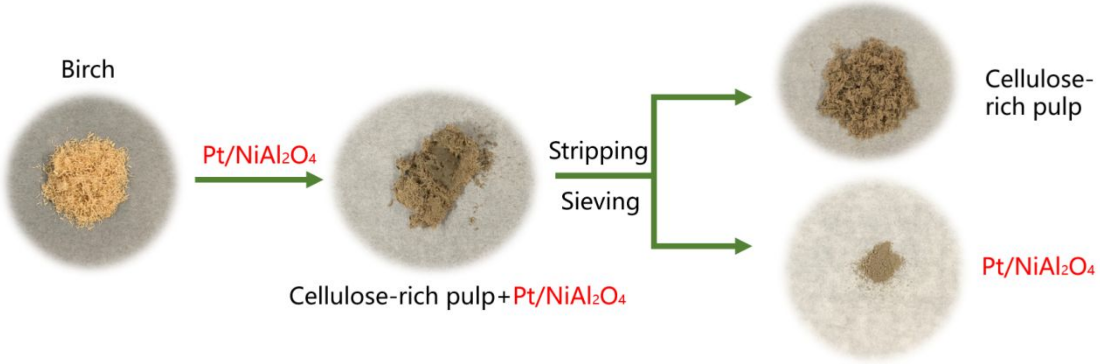
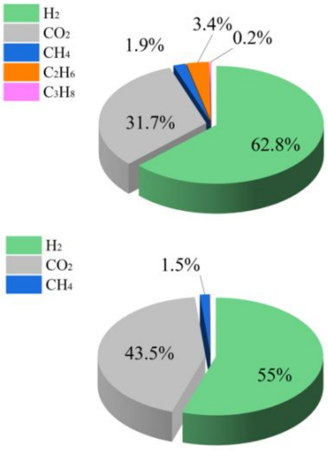


Figure S7. The flow-process diagram of separation the catalyst and cellulose-rich pulp.



(a)

H_2 prodction	H_2 selectivity	Carbon yield
4668 μmol/g	76.5%	8.13%

(b)

H_2 prodction	H_2 selectivity	Carbon yield
227 μmol/g	60.9%	0.56%

Figure S8. Gas products analysis in APR by using xylan (a) and cellulose (b) as substrates over the $Pt/NiAl_2O_4$ catalyst.

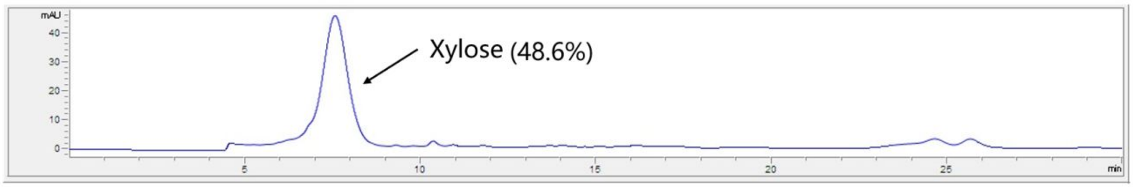


Figure S9. HPLC spectra of liquid phase after reaction without any catalyst.

Reaction conditions: birch sawdust (0.5 g), H_2O (10 mL), 140 ^oC, N_2 1 atm, 12 h.

Table S1. Physicochemical property of $Pt/NiAl_2O_4$ and $NiAl_2O_4$.

Catalyst	Metal content (wt%)	BET ($m^2\ g^{-1}$)	Pore diameter (nm)
$NiAl_2O_4$	-	59.3	18.6
$Pt/NiAl_2O_4$	1.7	61.6	17.2

Table S2. Compositional analysis of various lignocellulosic biomass.[a]

Samples	Cellulose (wt%)	HemiCellulose (wt%)	AIL (wt%)	AIL (wt%)	Total (wt%)
Birch	43.6	18.4	23.6	0.4	86.0
Poplar	45.3	22.1	20.1	0.8	87.5
Beech	41.1	19.4	21.2	0.5	82.2
Pine	47.6	9.3	29.4	0.6	86.9
Cornstalk	37.6	16.4	11.7	0.4	66.1

Note: Biomass compositions were determined according to standard analytical procedure (NREL/TP-510-42618).[3] The biomass powders (60-mesh) were extracted with toluene/ethanol (2:1, v/v) in a Soxhlet instrument for 12 h, and then dried at 80 °C for 5 h. The mixture containing 300 mg of dried biomass and 3 mL of 72 wt% H_2SO_4 solution were stirred at 30 °C for 1 h, which was then diluted by adding 84 mL deionized water, and heated at 121 °C for 1 h in the high-pressure sterilizer. After the reactor was cooled to room temperature, the solid residue and solution were separated through filtration. The solid residue was dried at 110 °C to gain Klason lignin (AIL). The acid soluble lignin (ASL) in filtrate was analysed using UV spectra by recording the absorbance of the soluble fraction at 240 nm. Finally, the determination of carbohydrates in the aqueous soluble fraction was performed on HPLC system.

Table S3. Monomer concentrations in various lignins.[a]

Lignin	Concentration / μmol g^{-1}		
	S	G	H
Birch	2272	221	52
Poplar	670	450	22
Beech	1458	490	51
Pine	23	940	0
Cornstalk	612	33	0

[a]The monomer analysis of lignin was carried out via alkaline nitrobenzene oxidation (NBO) according to the previous literature.[4] The biomass powders (40 mg) was mixed with nitrobenzene (0.4 mL) and 2 M NaOH (7 mL) and reacted at 170°C for 2 h. Afterwards, the

reactor was cooled in ice water and 1 mL of freshly prepared ethyl vanillin (3-ethoxy-4-hydroxybenzaldehyde, EV) (5 µmol/mL) in 0.1 M NaOH solution was added to the reaction mixture as an internal standard. The mixture was transferred to a 100 mL separatory funnel and washed three times with 15 mL of dichloromethane. The remaining aqueous layer was acidified with 2 M HCl, until the pH was below 3.0 and extracted twice with 20 mL of dichloromethane and 20 mL of diethyl ether. The combined organic layer was washed with deionized water (20 mL) and dried over Na_2SO_4. After filtration, the filtrate was collected in a 100 ml pear shaped flask and dried under reduced pressure. For the TMS (trimethylsilyl) derivatization step, NBO-products were washed with pyridine (3 × 200 µL) into a GC vial and BSTFA (150 µL) was added. The mixture was heated to 50°C for 30 min. The silylated NBO-products were analysed by GC-MS (Agilent 7890A) and quantitatively analysed by GC (Agilent 7890B) with a flame ionization detector, both quipped with HP-5 capillary columns.

Table S4. SCF of lignocellulose through amplification.[a]

Lignin-oil[b] (wt%)	Monomers yields[c] (wt%)	Monomer content in lignin oil[d] (wt%)	Molar yields of monomers[e] (mol%)	H_2 in the Gas (µmol /g)
22.8	39.2	41.2	82.1	319

[a] Reaction conditions: birch sawdust (5 g), Pt/$NiAl_2O_4$ (1 g), solvent (100 mL), 140 °C, N_2 1 atm, 24 h. [b] Based on the mass of lignocellulosic biomass. [c] The yields of monomers is based on Klason lignin content of 24 wt% from birch. [d] Based on the mass of lignin oil. [e] The mole yields of monomers is based on the mole of lignin monomers in lignocellulosic biomass.

Table S5. Comparison of reductive catalytic fractionation results over different catalyst in literatures.

Catalyst	Reaction conditions					Primary monomers[a]	Total monomers yield	Delignification	Sugar retention	Ref.
	Biomass	Catalyst dosage	Solvent	Atmosphere	Temp./Time					
RuN/ZnO/C (Ru, 0.12 wt%)	Birch (0.25 g)	0.025 g	MeOH (15 mL)	H_2 (3 Mpa)	240 ^{o}C/4 h	Pr-G; Pr-S	46.4 wt%	95 wt%	C6 (96 wt%)/ C5 (72 C%)	[5]
Pt/γ-Al_2O_3 (Pt, 1 wt%)	Birch (2 g)	0.5 g	MeOH/H_2O (40 mL)	N_2 (3 atm)	230 ^{o}C/3 h	Pr-S; Pe-S	49 wt%	94 wt%	C6 (41 wt%)/ C5 (<1 wt%)	[6]
Pd/CN_x (Pd, 0.25 wt%)	Birch (3 g)	0.45 g	MeOH (60 mL)	H_2 (3 Mpa)	250 ^{o}C/3 h	Pr-G; Pr-S; Pe-S	52.7 C%	87.1 wt%	84.2 wt%	[7]
Pd/C (Pd, 5 wt%)	Poplar (2 g)	0.2 g	MeOH (40 mL) H_3PO_4 (5 g/L)	H_2 (2 Mpa)	200 ^{o}C/3 h	POH-G; POH-S	42 wt%	96 wt%	C6 (91 wt%)/ C5 (27 wt%)	[8]
Ru/C (Ru, 5 wt%)	Birch (2 g)	0.3 g	MeOH (40 mL)	H_2 (3 Mpa)	250 ^{o}C/6 h	Pr-G; Pr-S	52 C%	92 wt%	C6 (95 wt%)/ C5 (47 wt%)	[9]
Ni/C (Ni, 10 wt%)	Birch (2 g)	0.1 g	MeOH (40 mL)	Ar (1 atm)	200 ^{o}C/6 h	Pr-G; Pr-S	54 wt%	-	-	[10]
Ni_1-Fe_1/C (Ni, 5 wt%)	Birch (0.5 g)	0.05 g	MeOH (10 mL)	H_2 (2 Mpa)	200 ^{o}C/6 h	Pr-G; Pr-S	39.5 wt%	-	-	[11]
Pt_1Ni/C (Pt, 0.3 wt%)	Birch (0.1 g)	0.02 g	MeOH (5 mL)	H_2 (5 Mpa)	300 ^{o}C/18 h	Pr-G; Pr-S	43 wt%	-	-	[12]
Co-phen/C (Co, 0.45 wt%)	Birch (0.2 g)	0.03 g	MeOH/H_2O (6 ml) HCOOH/Na	Ar (1 atm)	200 ^{o}C/4 h	Pr-G; Pr-S; Pe-G; Pe-S	34 wt%	-	-	[13]
Cu20-PMO (Cu, 15.4 wt%)	Poplar (1 g)	0.2 g	MeOH (10 mL)	H_2 (4 Mpa)	180 ^{o}C/18 h	Pr-G; Pr-S; POH-G; POH-S	36 wt%	-	-	[14]
Pt/$NiAl_2O_4$ (Pt, 2 wt%)	Birch (0.5 g)	0.1 g	H_2O (10 mL)	N_2 (1 atm)	140 ^{o}C/24 h	Pr-G; Pr-S	46.6 wt%	95 wt%	C6 (91 wt%)/ C5 (36 wt%)	This work

[a]Primary monomers:

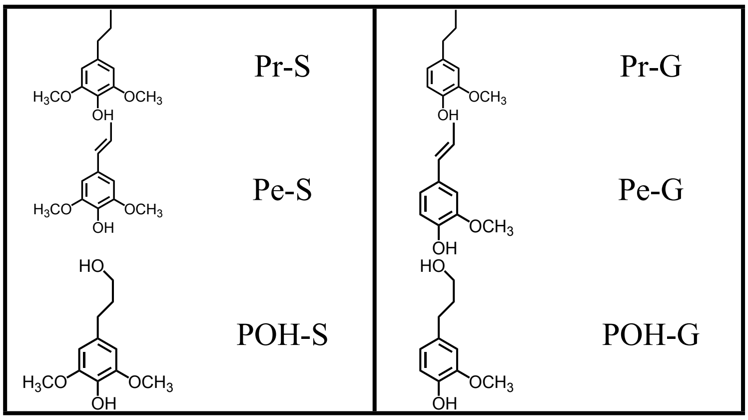


Table S6. Control experiment of SCF over the $Pt/NiAl_2O_4$ catalyst using cellulose as substrate.[a]

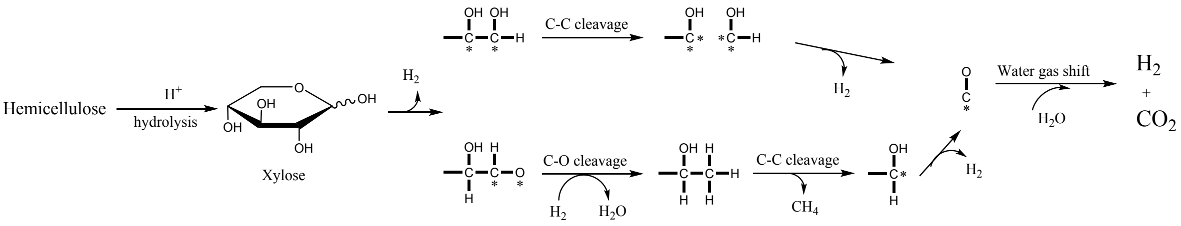
The mass of cellulose before reaction (g)	The mass of cellulose after reaction (g)	Retention (wt%)
0.2 g	0.18	90

[a] Reaction conditions: cellulose (0.2 g), $Pt/NiAl_2O_4$ (0.1 g), H_2O (10 mL), 140 °C, N_2 1 atm, 12 h.

Table S7. Monomers distribution and yields of SCF over the $Pt/NiAl_2O_4$ catalyst with different substrates.[a]

Substrates	Phenolic monomers yield (wt%)					Total(wt%)
	Er-G	Pr-G	Er-S	Pe-S	Pr-S	
Lignin+Xylan	-	0.3	5.7	-	1.9	7.9
Lignin+Xylose	-	3.2	3.1	1.6	11.6	19.5
Lignin+Cellulose	-	trace	1.1	-	1.1	2.2
Lignin	-	trace	0.9	-	0.8	1.7

[a] Reaction conditions: lignin (0.1 g) or lignin (0.1g) + xylan/xylose/cellulose (0.2 g), $Pt/NiAl_2O_4$ (0.1 g), H_2O (10 mL), 140 °C, N_2 1 atm, 12 h.



Scheme S1. Possible routes for hemicellulose to produce H_2 and CO_2

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