Supporting information

Selective cleavage of lignin model compounds and lignin without external hydrogen catalyzed by heterogeneous nickel catalysts

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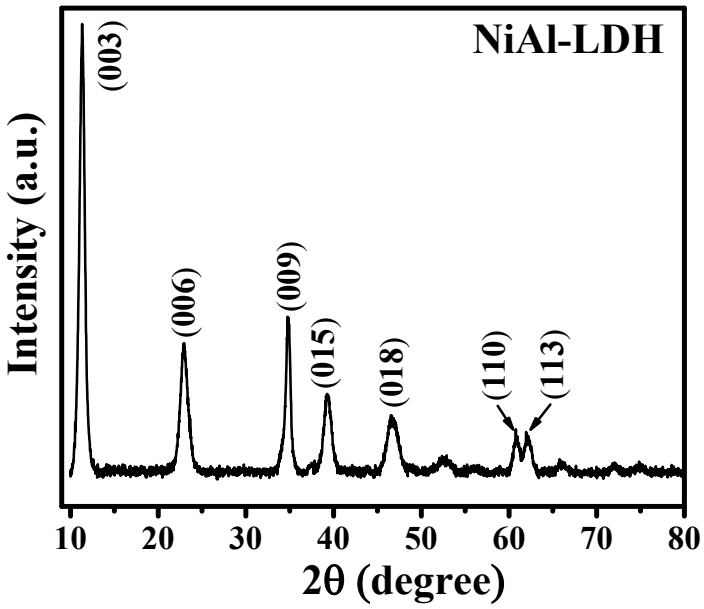


Figure S1. XRD patterns of the NiAl-LDH sample.

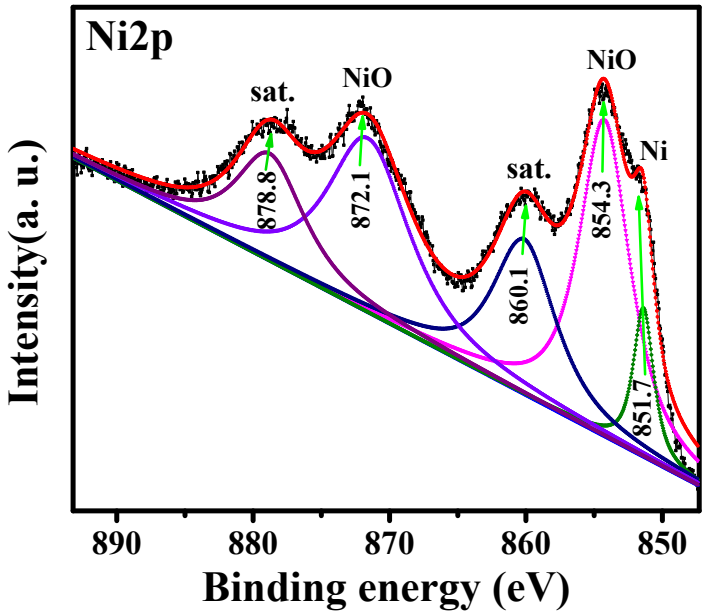


Figure S2. XPS spectra of the Ni/Al2O3-600 catalyst.

Table S1. Physicochemical properties of various catalysts.

Entry	Catalyst	Ni wt.%[a]	Ni crystallite size (nm)[b]	Surface Area(m^2/g)	Average Pore Diameter (nm)
1	Ni/Al_2O_3-500	56.15	5.5	121.57	12.99
2	Ni/Al_2O_3-550	56.97	5.8	110.15	13.70
3	Ni/Al_2O_3-600	61.42	6.4	104.16	14.36
4	Ni/Al_2O_3-650	61.45	8.6	83.93	16.79
5	Ni/Al_2O_3-700	61.50	10.2	83.86	17.07

Table S2. The results of the transfer hydrogenation of benzyl phenyl ether with different hydrogen donors.

Entry	Solvent	Conversion (%)	Yield (%)			
			Toluene	Cyclohexanol	Cyclohexanone	Phenol
1	Ethanol	1.8	1.8	0.2	-	1.6
2	*n*-Propanol	4.3	4.3	-	-	4.3
3	*n*-Butanol	4.2	4.2	-	0.3	3.9
4	*Iso*-propanol	100	100	92.3	0.9	6.8
5	2-Butanol	0	-	-	-	-

Reaction conditions: benzyl phenyl ether (α-O-4) (185 mg, 1 mmol), Ni/Al_2O_3-600 (20 mg), solvent (10 mL), 160 °C, 3 h, stirring at 1000 rpm.

Table S3. The results of the cleavage of the three model compounds. [a]

Entry	Substrate	Time (h)	Conversion (%)	Substrate consumption rate (mmol/$g_{cata.}$/h)	BDE (kJ·mol^{-1})	E_a (kJ·mol^{-1})
1	Benzyl phenyl ether	1	14.4	7.2	218	103
2	2-Phenylethyl phenyl ether	4	17.6	2.2	289	130
3	Diphenyl ether	6	18.7	1.6	314	147

[a] **Reaction conditions**: Substrate (1 mmol), Ni/Al_2O_3-600 (20 mg), solvent (10 mL), 1 MPa N_2, 130 °C, stirring at 1000 rpm.

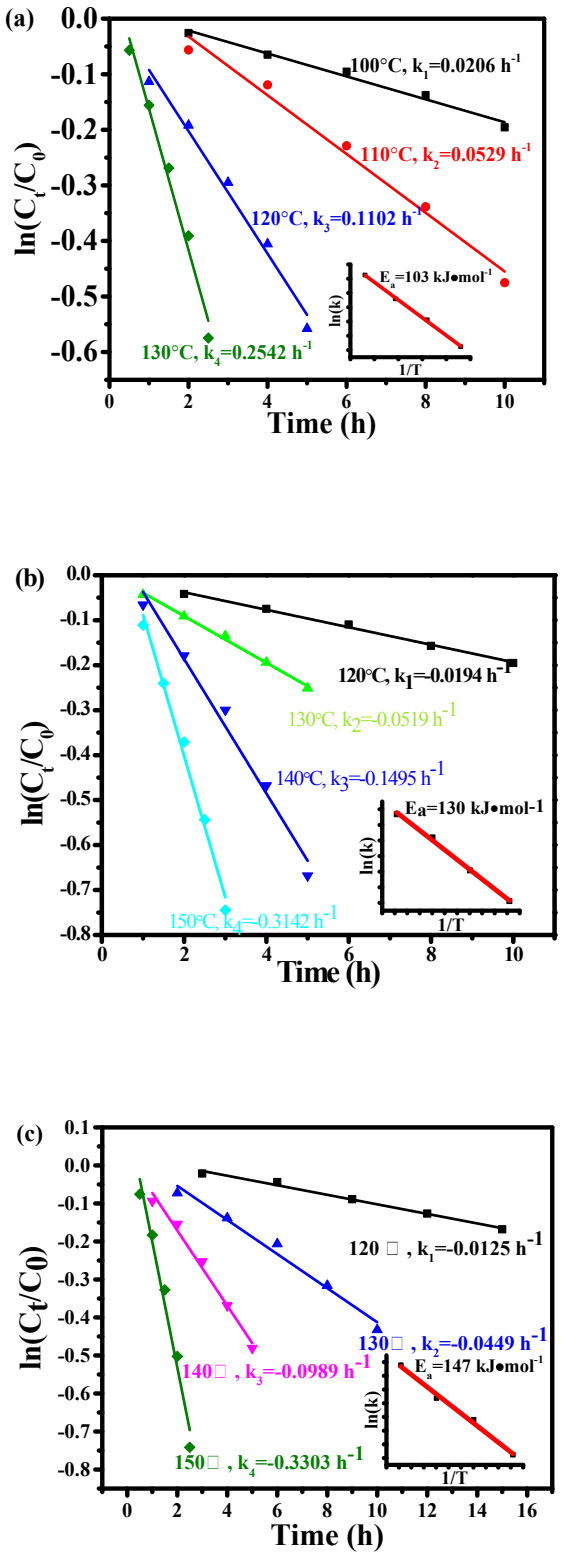
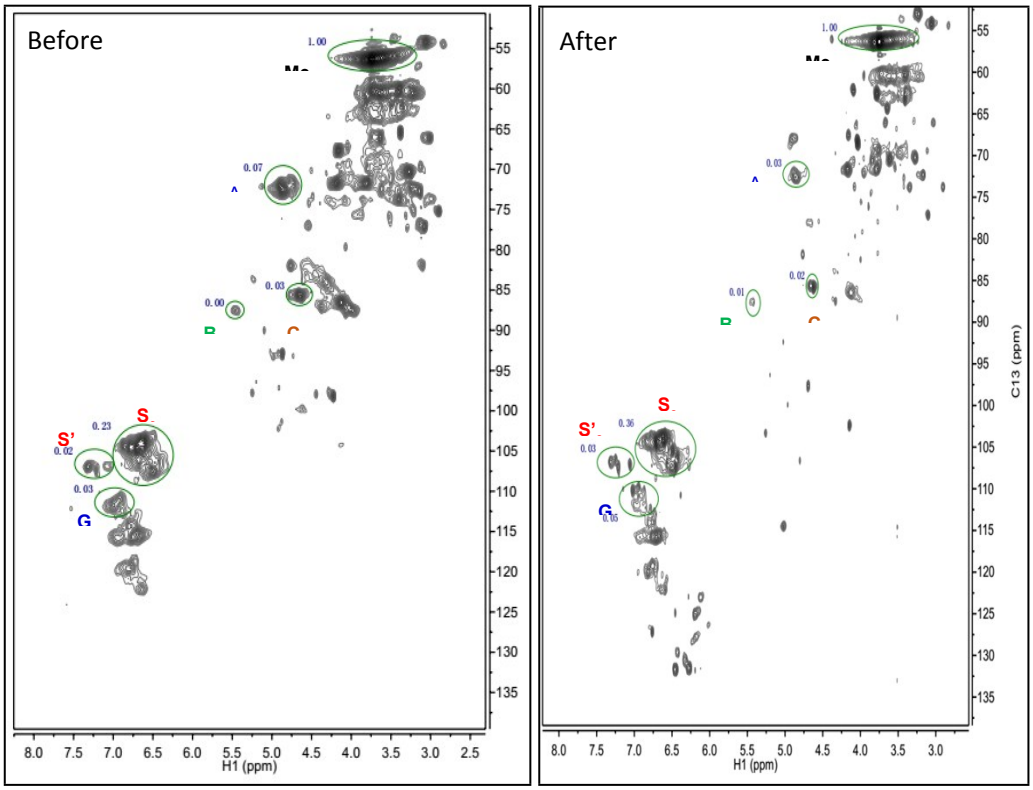


Figure S3. Kinetics studies and the activation energies of the transfer cleavage of the three the three model compounds. (a) Benzyl phenyl ether; (b) 2-Phenylethyl phenyl ether; (c) Diphenyl ether.



Units/100 C_9	Before reaction	After reaction
A	45	12
B	6	4
C	10	8
LBHK	13	3

Equation: A (or B or LBHK) /100 C_9= Aα (or Bα or LBHK-γ)*100/[($S_{2,6}$ +$S'_{2,6}$)/2 + G_2]

C /100 C_9= Cα/2*100/[($S_{2,6}$ +$S'_{2,6}$)/2 + G_2]

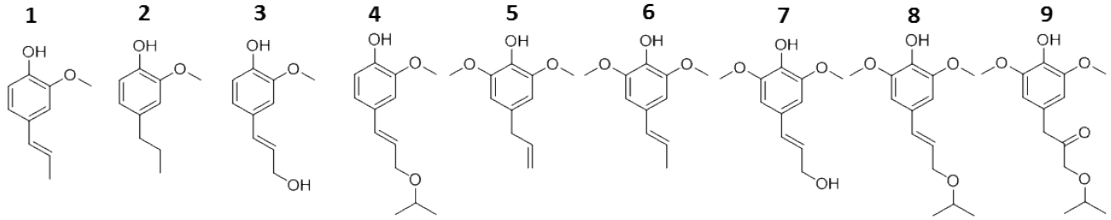
For example in Figure S3: Before reaction-lignin

A /100 C_9=0.07*100/[(0.23+0.02)/2+0.03]=45.16

Figure S4. Full 2D HSQC NMR spectra and the corresponding integration of linkages in beech lignin before and after reaction.

Table S4. Depolymerisation results of beech lignin over Ni/Al_2O_3-600.

1	2	3	4	5	6	7	8	9	Identified monomer yield %	Total oil yield %
0.58	0.49	1.60	1.61	0.85	2.37	1.70	2.70	1.48	13.38	69.20



Reaction conditions: Beech lignin: 100mg; Ni/Al_2O_3: 30 mg; isopropanol: 20 mL; 170 ^oC; 12 h; 1 MPa N_2.