Catalytic lignin valorization over HSZ-supported CuNiAl-based catalysts with microwave heating

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Table S1 ICP results of CuNiAl/HSZ catalysts

Catalyst	Sample quality m_0 (g)	Constant volume V_0 (mL)	Element	Element concentration C_o (mol/L)	The amount of elemental matter (mol)
HT/HSZ-640	0.0591	10	Al	0.44	0.0044
	0.0591	10	Cu	0.31	0.0031
	0.0591	10	Ni	0.94	0.0094
HT/HSZ-660	0.0955	10	Al	0.39	0.0039
	0.0955	10	Cu	0.27	0.0027
	0.0955	10	Ni	0.91	0.0091
HT/HSZ-690	0.0559	10	Al	0.45	0.0045
	0.0559	10	Cu	0.34	0.0034
	0.0559	10	Ni	0.92	0.0092

Table S2 Si/Al molar ratio before and after CuNiAl mix-oxide incorporation

Catalysts	HSZ-640	HSZ-660	HSZ-690
Si/Al ratio(before)	17	28	241
Si/Al ratio(after)	18	30	240

Table S3 CO_2-TPD result of CuNiAl-HT and CuNiAl/HSZ materials

Catalyst	Temperature at maximum (℃)	Quantity(mmol/g)
CuNiAl-HT	109.4	0.0772
HT/HSZ-640	102.7	0.0713
HT/HSZ-660	93.5	0.0561
HT/HSZ-690	91.7	0.0807

Table S4 Effect of basic catalysts on molecular weights and HHV of bio-oil

Entry	Catalysts	MW		Elemental composition (wt.%)							HHV
		M_n	M_w	C	H	O	N	S	O/C	H/C	
1	HT/HSZ-660[a]	485.3	628.8	49.65	13.53	36.52	0.19	0.11	0.55	3.27	30.15
2	HT/HSZ-660[b]	492.1	639.2	48.82	12.53	39.52	0.10	0.13	0.61	3.06	28.17

Reaction conditions: a- metal mixtures supported on acidic HSZ; b-metal mixtures supported on basic HSZ, HT (Cu/Ni/Al ratio of 1.5:4.5:2); HHV (MJ/kg) = (34C+124.3H+6.3N+19.3S-9.8O)/100, where C, H, N, S, and O are the weight percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen.

Table S5 Effect of Cu in CuNiAl-HT/HSZ-660 catalyst

Entry	Catalysts	MW		Elemental composition (wt.%)							HHV
		M_n	M_w	C	H	O	N	S	O/C	H/C	
1	CuNiAl-HT/HSZ-660	485.3	628.8	49.65	13.53	36.52	0.19	0.11	0.55	3.27	30.15
2	NiAl-HT/HSZ-660	501.1	645.2	49.80	12.78	38.65	0.18	0.12	0.60	3.09	28.22

Table S6 Mass balance of reaction [a]

Catalyst	Bio-oil	Char	Gas product
HT/HSZ-660	0.83g	0.15g	0.02g

[a] Reaction condition: 1 g lignin, 0. 05 g catalyst and 4 g solvent. In the end of the reaction, the mixture including of solvent, bio-oil and solid residue was concentrated on the rotary evaporator to remove the solvent.

Table S7 Chemical and physical properties of calcined HT/HSZ-640, HT/HSZ-660 and HT/HSZ-690.

Catalyst	HT/HSZ-640	HT/HSZ-660	HT/HSZ-690
S_{BET}^a (m^2/g)	168.8	173.4	177.3
Mean pore size[a](nm)	15.7	16.4	16.2
Average metal size[b](nm)	14.8	14.5	14.2
Cu/Ni ratio[c]	0.1965	0.2478	0.3247
(Cu+Ni)/Al ratio[c]	2.96	2.95	2.95
Al (wt%)	4.7	4.9	4.9
Cu (wt%)	2.9	2.8	3.1
Ni (wt%)	9.8	9.7	9.6

a-Evaluated from N_2 adsorption-desorption isotherms; b-Calculated by TEM; c-Calculated by ICP analysis.

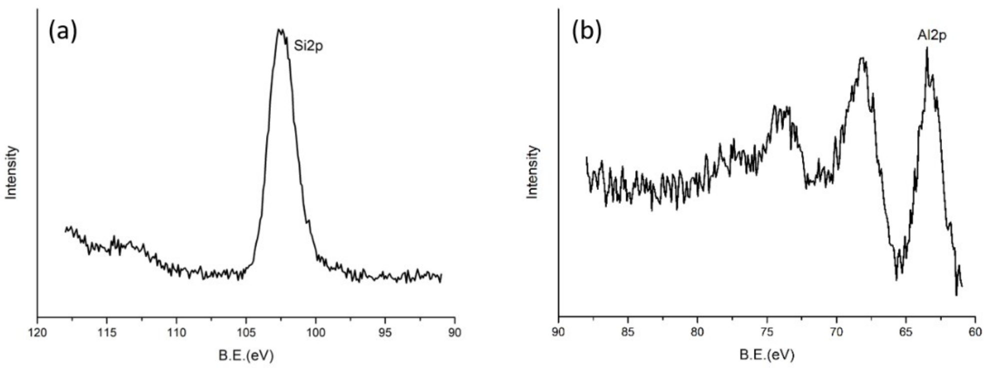

Fig. S1 XPS analysis for CuNiAl-HT/HSZ-600 catalyst (a) Si2p, (a) Al2p.

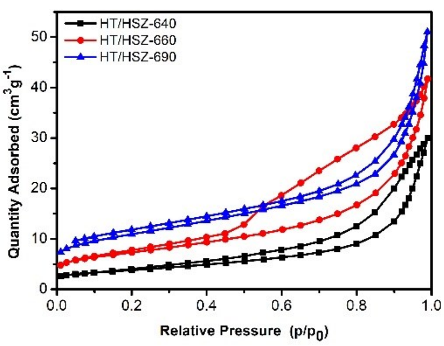

Fig. S2 N_2 adsorption isotherms of HT/HSZ-640, HT/HSZ-660 and HT/HSZ-690.