Supporting information

Highly Efficient Hydrogenation of Lignin over Ni-Based Alloy Catalysts

Xiaolong Chen [1], Hongli Wu [1,*], Peipei Zhang [2], Weina Zhang [1], Wei Jia [3,*], Pengfei Gao [1], Guo Tang [3],
Fengyun Ma [3], Qinglong Xian [3] and Noritatsu Tsubaki [4,*]

[1] Xinjiang Key Laboratory of Agricultural Chemistry and Biomaterials, College of Chemistry and Chemical Engineering, Xinjiang Agricultural University, Urumqi 830052, China; cxiaolong929@163.com (X.C.); zwn163yx@163.com (W.Z.); gpf15276713467@163.com (P.G.)
[2] China National Offshore Oil Corporation (CNOOC)Institute of Chemical & Advanced Materials, Beijing 102209, China; zhangpp15@cnooc.com.cn
[3] Xinjiang Key Laboratory of Advanced Functional Materials, Autonomous Region, College of Chemistry, Xinjiang University, Urumqi 830046, China; tg18228484851@163.com (G.T.); ma_fy@126.com (F.M.); jlcsxian@163.com (Q.X.)
[4] Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan
* Correspondence: hongli58@xjau.edu.cn (H.W.); jia3816892@163.com (W.J.); tsubaki@eng.u-toyama.ac.jp (N.T.)

Analysis of lignin by GC-MS

Gas chromatography–mass spectrometry (GC–MS) (Agilent 6890-5973) and gas chromatography–flame ionization detection (GC–FID) (Agilent 6890) were employed for the qualitative and quantitative analyses of the monomers in the liquid-phase products, respectively. A TG-5 MS column was used, and both GCs instruments operated under identical conditions. The injector temperature was 270 ℃, the ion source temperature was 230 ℃, the MS quadrupole was 150 ℃, and the split ratio was 10:1. The initial temperature was held at 45 ℃ for 2 min, then increased to 250 ℃ at a rate of 10 ℃/min for 2 min, followed by an increase to 280 ℃ at 5 ℃/min for 5 min. For the mass spectrometry detector, a solvent delay of 3 min was applied, and the mass detector was set to scan from 10 to 500 m/z.

An internal standard method was used to quantify the monomers, using

acetophenone as an internal standard. Due to the uncertainty of the response factor for the unknown monomer, the average response factor of all identified monomers was used as a representative value for the unknown species. To ensure reliable monomer yield measurements, all reported values represent the average of three independent experimental runs.

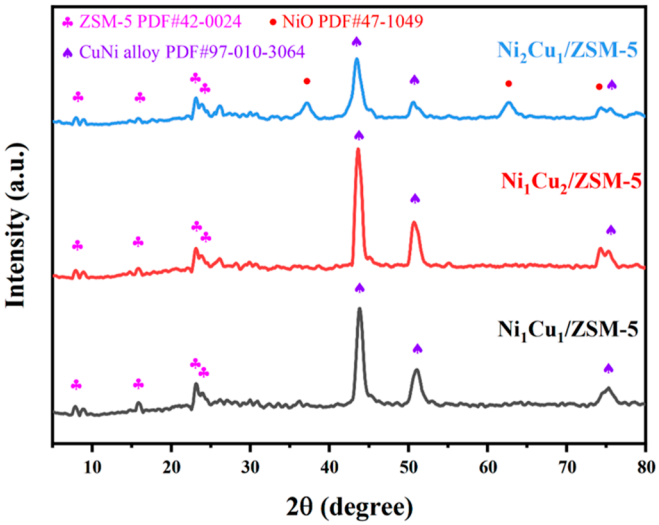


Figure S1. XRD patterns of Ni_1Cu_1/ZSM-5, Ni_1Cu_2/ZSM-5 and Ni_2Cu_1/ZSM-5 catalysts.

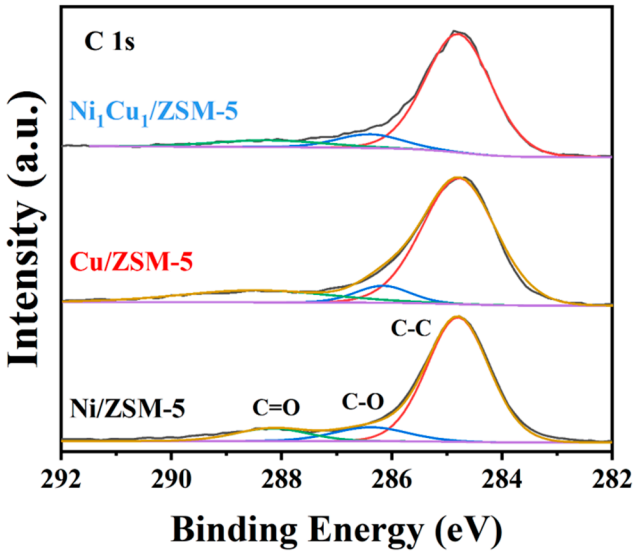


Figure S2. XPS C 1s spectra of Ni/ZSM-5, Ni_1Cu_1/ZSM-5, Cu/ZSM-5 catalysts.

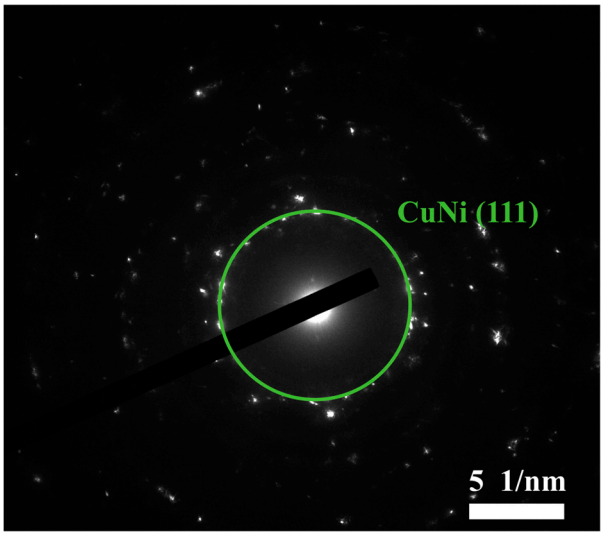


Figure S3. SEAD pattern of Ni_1Cu_1/ZSM-5 catalysts.

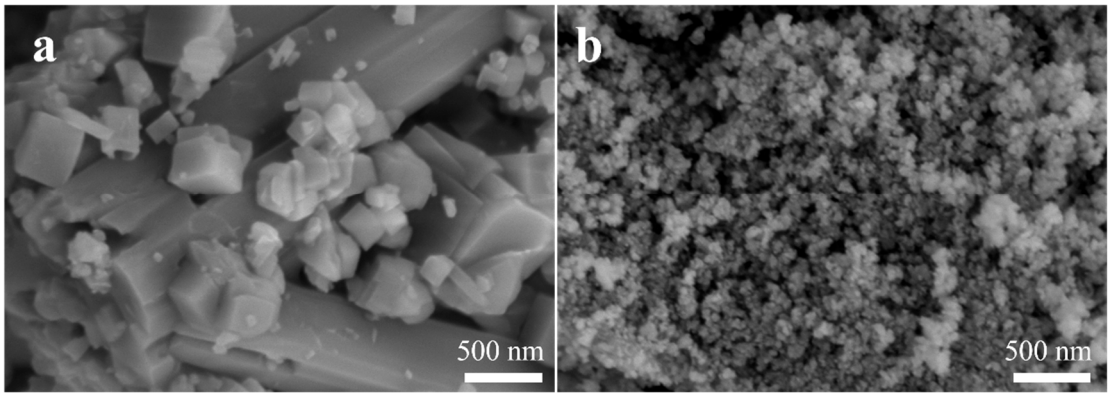


Figure S4. SEM images of ZSM-5 and Ni.

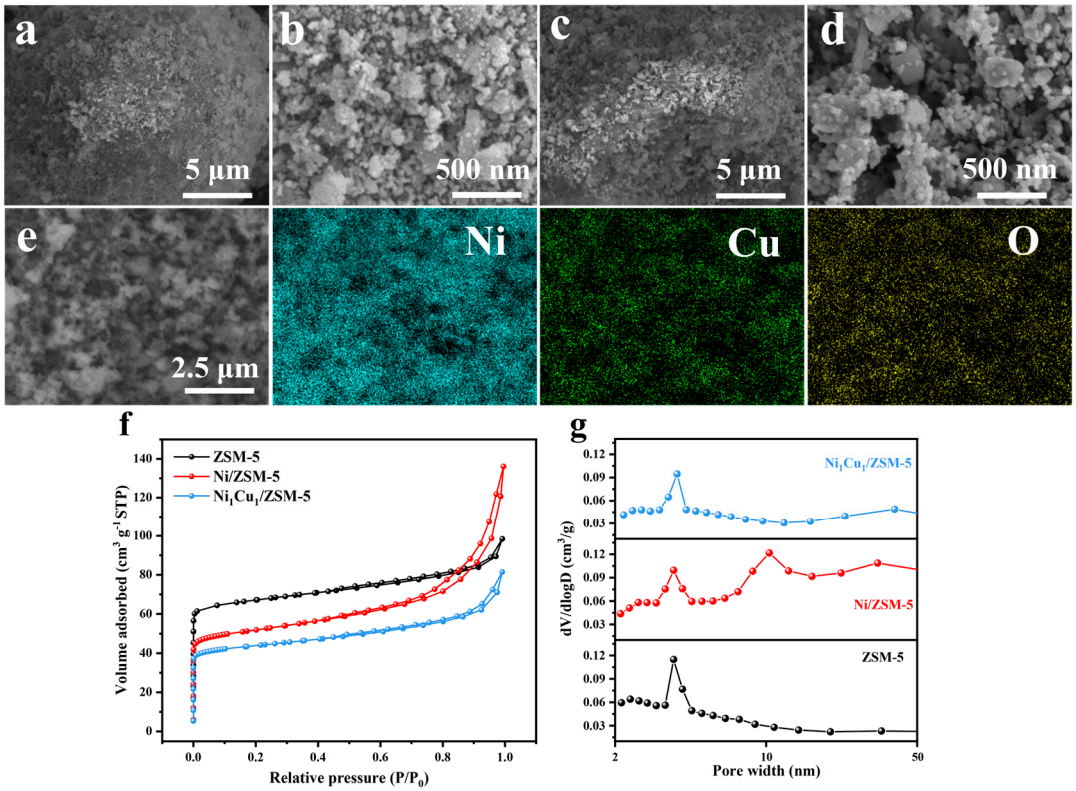


Figure S5. SEM images of (a), (b) Ni/ZSM-5 and (c), (d) Ni_1Cu_1/ZSM-5; (e) Elemental distribution SE images of Ni_1Cu_1/ZSM-5 catalyst; (f) N_2 adsorption–desorption isotherms and (g) Pore size distributions of ZSM-5, Ni/ZSM-5, and Ni_1Cu_1/ZSM-5.

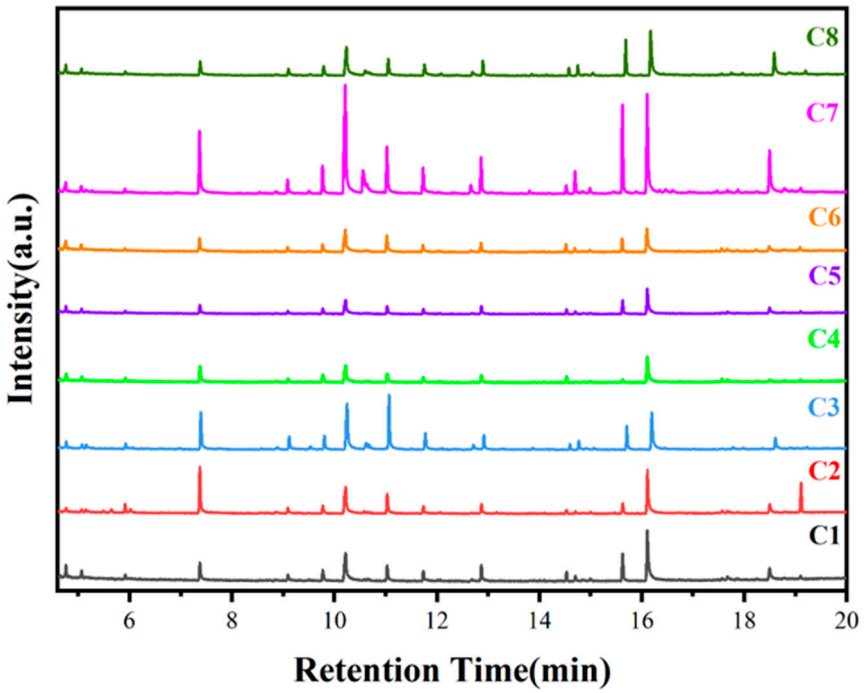


Figure S6. Cyclic GC-MS of Ni_1Cu_1/ZSM-5 catalyst during lignin hydrodeoxygenation reaction.

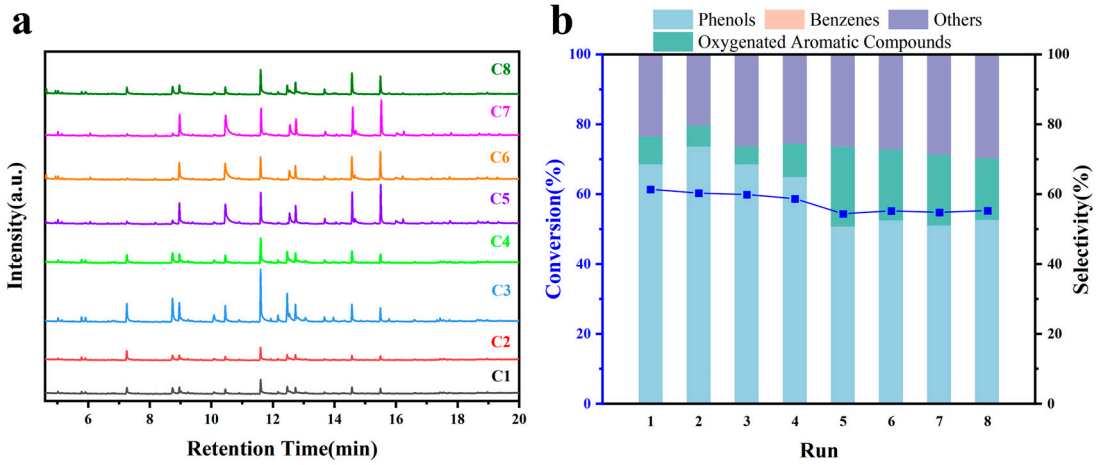


Figure S7. Analysis of the cyclic performance of Ni/ZSM-5 catalyst in lignin hydrodeoxygenation reaction.

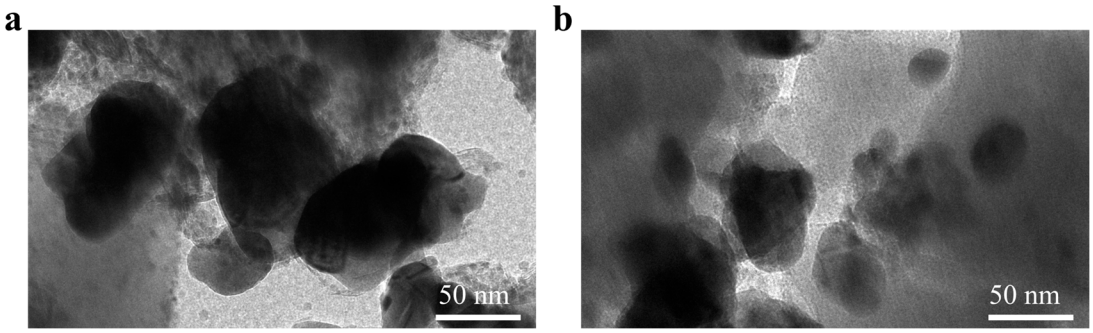


Figure S8. (a) Ni/ZSM-5 and (b) Ni_1Cu_1/ZSM-5 after the reaction (TEM images).

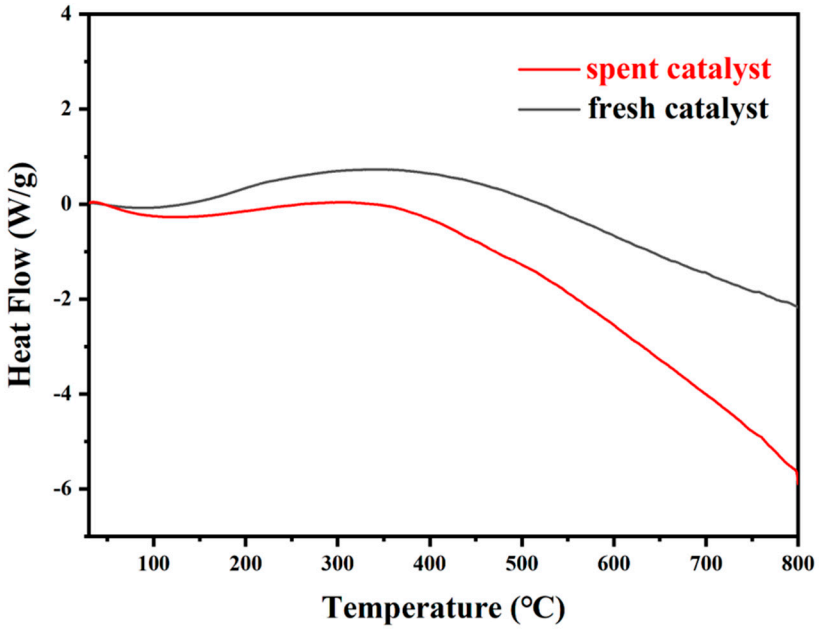


Figure S9. DSC curves of the fresh and spent Ni_1Cu_1/ZSM-5 catalysts.

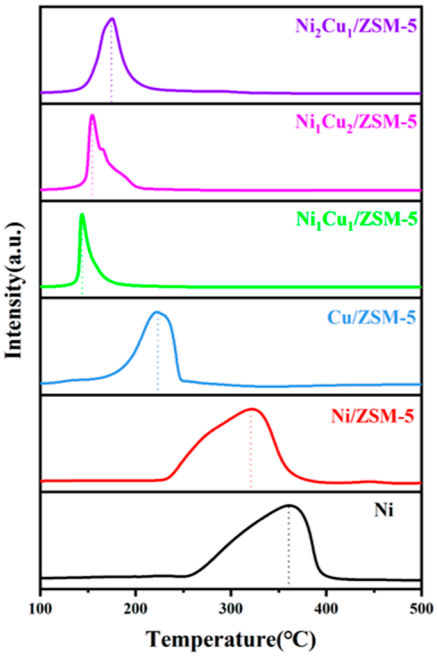


Figure S10. H_2-TPR profiles of Ni, Ni/ZSM-5, Cu/ZSM-5, Ni_1Cu_1/ZSM-5, Ni_1Cu_2/ZSM-5 and Ni_2Cu_1/ZSM-5 catalysts.

Table S1. ICP-OES results of Ni/ZSM-5, Ni_1Cu_1/ZSM-5, Cu/ZSM-5 catalysts.

Sample	Ni loading (at%)	Cu loading (at%)
Ni/ZSM-5	5.15	/
Ni_1Cu_1/ZSM-5	2.38	2.46
Cu/ZSM-5	/	4.84

Table S2. Binding energy of different catalysts (Ni and Cu).

Catalyst	Ni (eV)				Cu (eV)			
	Ni^0 $2p_{3/2}$	Ni^{2+} $2p_{3/2}$	Ni^0 $2p_{1/2}$	Ni^{2+} $2p_{1/2}$	Cu^0 $2p_{3/2}$	Cu^{2+} $2p_{3/2}$	Cu^0 $2p_{1/2}$	Cu^{2+} $2p_{1/2}$
Ni/ZSM-5	852.4	854.9	870.0	872.8	/	/	/	/
Ni_1Cu_1/ZSM-5	852.6	855.0	870.2	872.9	932.4	933.7	952.3	953.6
Cu/ZSM-5	/	/	/	/	932.6	934.5	952.5	954.4

Table S3. Textural analysis of ZSM-5, Ni/ZSM-5, Cu/ZSM-5 and Ni_1Cu_1/ZSM-5.

Sample	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
ZSM-5	268.50	0.15	2.87
Ni/ZSM-5	208.48	0.20	4.79
Cu/ZSM-5	184.60	0.20	5.23
Ni_1Cu_1/ZSM-5	178.51	0.12	3.62

Table S4. Lignin hydrogenation performance with different catalysts.

Entry	Catalyst	Conversion	Selectivity			
			Phenols	Benzenes	OXY	Others
1	ZSM-5	32.8	10.0	21.9	4.7	63.4
2	Ni	47.1	8.4	21	0.0	70.6
3	Cu	46.5	30.7	59.2	3.8	6.3
4	Ni_1Cu_1	56.2	12.1	32.1	6.7	49.1
5	Ni_1Cu_2	52.8	42.3	17.4	4.0	36.3
6	Ni_2Cu_1	55.4	34.6	5.9	3.6	55.9

Table S5. Effect of Ni/Cu molar ratios on the hydrogenation performance of NiCu/ZSM-5 catalysts.

Entry	Catalyst	Conversion	Selectivity			
			Phenols	Benzenes	OXY	Others
1	Ni/ZSM-5	49.3	12.8	43.5	0.0	43.7
2	Cu/ZSM-5	57.1	20.7	69.2	3.8	6.3
3	Ni_1Cu_2/ZSM-5	59.4	50.7	34.4	10.4	4.5
4	Ni_2Cu_1/ZSM-5	58.6	10.4	44.8	32.0	12.8

Table S6. Hydrodeoxygenation of Lignin to Phenolic Compounds over Various Metallic Catalysts.

Entry	Catalyst	Phenolic yield (%)	Ref
1	3% Cu@MIL-101	10.4	[38]
2	NiCo/C（5+5wt%）	16.4	[14]
3	Ni/LNC	22.1	[39]
4	Fe-Mo-P	34.9	[40]
5	Ni-Fe-Mo_2C/AC	35.5	[41]
6	Ni/ZrP2.0	43.7	[42]
7	Ni_5Fe_2/TiN	45.2	[43]
8	Ni-Co/C	53.1	[44]
9	15Ni/SA-$Zr_{0.5}$	53.4	[18]
10	9.0Fe-1.0Pd/HZSM-5	57.5	[45]
11	Ni_1Cu_1/ZSM-5	58.9	This work

Table S7. Precursor weights of NiCu catalysts with different Ni/Cu molar ratios.

Ni/Cu Molar Ratio	Weight of $(Ni(NO_3)_2 \cdot 6H_2O)$(g)	Weight of $(Cu(NO_3)_2 \cdot 3H_2O)$(g)
1:0	8.72	0
1:1	4.36	3.62
1:2	2.91	4.83
2:1	5.82	2.42
0:1	0	7.25