Supporting information

Facile depolymerization of lignin into phenolics via self-hydrogen

transfer hydrogenolysis over skeletal CuZnAl catalyst

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1. Catalyst preparation

CuZnAlO_x catalysts

The lignin dimers were prepared according to the reported procedure^[S1]. The CuZnAlO_x catalysts were synthesized via the traditional co-precipitation method by using Na₂CO₃ as precipitator. A certain amounts of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, and Al(NO₃)₃·6H₂O were dissolved in 50 mL of deionized water filled in a three-neck flask to make a total metal ion concentration of 2 mol/L. An aqueous solution mixture of sodium carbonate (2 mol/L) was then added dropwise at 60 °C under vigorous stirring until the pH value reached 9.0. The resulting precipitate was aged in the mother liquor at the same temperature overnight to form the hydrotalcite-like compound (HTLcs). The product was washed with deionized water at room temperature and dried at 100 °C overnight. The CuZnAl oxide catalysts were then obtained by thermal decomposition of the HTLcs precursor in air at 600 °C at a rate of 2 °C min⁻¹ for 3 h. Then, the CuZnAl oxide catalysts were reduced by 20 vol% H₂ in N₂ at 280 °C for 3 h.

2. Lignin model compound preparation

Preparation of 2-(2-Methoxyphenoxy)-phenethyl alcohol.



The lignin dimers were prepared according to reported procedures^[S2]. A 500 mL round bottom flask equipped with a reflux condenser and a dropping funnel was charged with guaiacol (27 mmol) and potassium carbonate (38 mmol) in acetone (125 mL) and stirred at room temperature. To this solution, 2-bromoacetophenone (25 mmol) in acetone (25 mL) was added dropwise over 30 min at room temperature. The resulting suspension was stirred at reflux for 6 h, after the suspension was filtered and concentrated in vacuo. The crude product was purified by recrystallization as a white solid.



A round bottom flask was charged with 2-(2-methoxyphenoxy)-acetophenone (20 mmol) and tetrahydrofuran (125 mL). Sodium borohydride (22 mmol) was added to the solution in small portions at 25 °C. After stirring for 5 h, the suspension was quenched with saturated aqueous NH₄Cl (75 mL), followed by the addition of Ethylacetate (75 mL). After separation, the organic phase was washed with H₂O, dried over Mg₂SO₄, filtered and the solvent was evaporated under vacuum.

Lignin extraction

Birch organosolv lignin was extracted according to reported works^[S3]. 60 g of the dried birch wood and 430 mL 1,4-dioxane with the 50 mL solution of HCl (2mol L⁻¹) were added to a 1 L round-bottom flask. The mixture was refluxed for 90 min under a nitrogen atmosphere, and cooled to room temperature. The residue was removed by filtration and the filtrate was concentrated. The resulting concentrate was then added into 2 L water to get precipitate. The precipitate was collected by filtration and washed with a large number of water until the filtrate was neutral. The yield of crude birch lignin with dried was 9 g (15 wt%). The resulting crude birch lignin was dissolved in 60 mL solvent (acetone:water = 9:1) and the precipitated with 1.5 L of ice-cold water. The final lignin was collected by filtration, washed and dried under vacuum at 60 °C. The yield of purified birch lignin was \sim 6 g (10 wt%).

3. Depolymerization and yield calculations for native lignin

The catalytic conversion of lignin was carried out in an autoclave (15 mL). Lignin (200 mg), o-xylene (4 mL) and CuZnAl catalyst (500 mg) were loaded into autoclave and reacted at 200 °C, 4 MPa N_2 and 800 rpm for 24 h. At the end of the reaction, the react mixture was cooled down to room temperature and sampled for analysis. The mixture was filtered to remove the catalyst and solid residues, followed by multiple washing cycles to ensure complete transfer of residual products from the solid phase to the liquid phase. Subsequently, the liquid phase was concentrated through rotary evaporation to eliminate solvents, and the remaining liquid phase was weighed to determine the mass of the lignin oil. The obtained product was then dissolved in a fixed volume of ethyl acetate with the addition of naphthalene as an internal standard. The organic products were analyzed qualitatively by GC.

4. Supplementary figures



Figure S1. Schematic diagram of the preparation procedures of CuZnAl-x.



Figure S2. The TEM images of CuZnAl-0.5



Figure S3. The TEM images of CuZnAl-2.5



Figure S4. XPS spectra of Cu 2p of the CuZnAl alloy.



Figure S5. N₂ adsorption-desorption isotherms and Pore size distribution of CuZnAl alloy.

5. Supplementary tables

	M _n	$M_{\rm w}$	M_p	M_z
Lignin	2618	4028	2388	10520
Lignin oil	1270	1301	1101	1336

 Table S1. The GPC results of lignin and lignin oil.

Table S2. The reported systems for the STH of lignin model compounds.

Substrate	Catalyst	Conditions	Con.	Yield	Reference
2-Phenoxy-1- phenethanol	Pd ₁ Ni ₄ /MIL-100(Fe)	130 °C, 6 h, 1 atm N ₂ 1 mL H ₂ O	100	95	[S4]
2-Phenoxy-1- phenethanol	$ZnIn_2S_4$	42 °C, 4 h, 1 atm Ar 1 mL CH ₃ CN, 9.6 W blue LEDs (455 nm)	100	90	[85]
α-(2- methoxypheno xy)methyl- benzenemetha nol	Pt/NiAl ₂ O ₄	250 °C, 1 h, 2 MPa N ₂ 15 mL H ₂ O	95	80	[S6]
2-Phenoxy-1- phenethanol	Ag ₂ S(2%)@CdS	30 °C, 3 h, 1 atm Ar 1 mL CH ₃ CN, 5 W blue LEDs	100	95	[87]
2-Phenoxy-1- phenethanol	Pd-PdO/TiO ₂	120 °C, 1 h, 1 atm Ar 2 mL H ₂ O	95	81	[S8]
2-Phenoxy-1- phenethanol	Au-Pd/ZrO ₂	80 °C, 24 h, 1 atm Ar 2 mL of cyclohexane, 0.5 W·cm ⁻² intensity of visible light	98	95	[89]
2-Phenoxy-1- phenethanol	Ni-NDC-500	220 °C, 2 h, 2 MPa N ₂ 5 mL H ₂ O	99.9	99.9	[S10]
2-Phenoxy-1- phenethanol	NiCu/Al ₂ O ₃	200 °C, 2 h, 1 MPa N ₂ 20 mL n-hexane	95	95	[S11]
2-Phenoxy-1- phenethanol	CuZnAl-1.5	160 °C, 12 h, 1 atm N ₂ 3 mL o-Xylene	100	92	This work

			Yield (%)					
No.	Catalyst	Con. (%) -	phenol	acetophenone	PPE	α-СО-РРЕ		
1	30 mg CuZnAl-1.5	64	44	45	3	13		
2	60 mg CuZnAl-1.5	85	65	65	5	12		
3	90 mg CuZnAl-1.5	94	69	69	7	8		
4	120 mg CuZnAl-1.5	96	79	79	8	6		
5	150 mg CuZnAl-1.5	100	92	92	7	1		

Table S3. The effect of catalyst loading.

Reaction condition: 0.25 mmol α-OH-PPE, 160 °C, 12 h, 3 mL o-xylene.

No	colventa	C_{op} (9/)	Yield (%)				
INO.	solvents	Coll. (76) -	phenol	acetophenone	PPE	α-CO-PPE	
1	γ-GVL	0	0	0	0	0	
2	1,4-dioxane	0	0	0	0	0	
3	THF	7	4	5	1	0	
4	Ethyl acetate	21	10	8	7	4	
5	n-Hexane	53	37	40	3	8	
6	Water	57	54	49	1	0	
7	p-Xylene	99	87	88	10	3	
8	m-Xylene	100	91	90	9	1	
9	o-Xylene	100	92	92	7	1	

Table S4. The effect of reaction solvents.

reaction condition: 0.25 mmol α -OH-PPE, 150 mg CuZnAl-1.5 (wet weight), 160 °C, 12 h, 3 mL solvents.

N	T_{constant} (0C)	Con. (%) –	Yield (%)					
NO. 1	Temperature (°C)		phenol	acetophenone	PPE	α-CO-PPE		
1	110	43	29	29	2	10		
2	120	59	42	42	3	12		
3	130	75	57	57	6	8		
4	140	80	65	65	7	8		
5	150	99	82	86	7	6		
6	160	100	92	92	7	1		

 Table S5. The effect of reaction temperature.

reaction condition: 0.25 mmol *a*-OH-PPE, 150 mg CuZnAl-1.5 (wet weight), 12 h, 3 mL o-xylene.

Table S6.	The effect	of additives	on the	reaction.
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No	Catalyst	Con.	Yield (%)				
INO.	Catalyst	(%)	phenol	acetophenone	PPE	α-CO-PPE	
1	CuZnAl-1.5 (water)	63	55	51	2	5	
2	CuZnAl-1.5 (o-Xylene)	54	37	39	1	13	
3	CuZnAl-1.5 (o-Xylene) +100 µl water	64	47	49	7	2	
4	CuZnAl-1.5 (o-Xylene) +0 µl water	53	39	37	1	13	
5	CuZnAl-1.5 (o-Xylene) +30 µl water	55	41	42	1	9	
6	CuZnAl-1.5 (o-Xylene) +60 µl water	63	49	49	2	8	
7	CuZnAl-1.5 (o-Xylene) +0 mmol <i>p</i> -TSA	54	39	37	13	1	
8	CuZnAl-1.5 (o-Xylene) +10 ⁻⁸ mmol <i>p</i> -TSA	67	53	54	8	2	
9	CuZnAl-1.5 (o-Xylene) +10 ⁻⁷ mmol <i>p</i> -TSA	80	57	59	17	1	

reaction condition: 0.25 mmol α -OH-PPE, 150 mg CuZnAl-1.5 (wet weight), 160 °C, 1.5 h, 3 mL o-xylene.

			Yield (%)				
No.	Time (h)	Con. (%) -	phenol	acetophenone	PPE	α-СО-РРЕ	
1	0	0	0	0	0	0	
2	0.25	44	25	29	1	13	
3	0.75	63	40	43	1	16	
4	1	69	54	54	2	10	
5	2	75	63	63	2	8	
6	4	86	75	75	3	6	
7	6	91	79	79	5	5	
8	8	95	84	83	6	4	
9	10	96	85	86	7	2	
10	12	100	92	92	7	1	

Table S7. The Products distribution as a function of time.

Reaction condition: 0.25 mmol α -OH-PPE, 150 mg CuZnAl-1.5 (wet weight), 160 °C, 3 mL oxylene.

					Yield(%)			
Ent	Solvent	Catalyst	Time	Conv.(%)	D1 1	Acetop	Cyclohe	Ethylbe
ry					Phenol	henone	xanol	nzene
1	o-xylene	CuZnAl-1.5	12 h	0	0	0	0	0
ſ		CuZnAl-1.5	10 h	0	0	0	0	0
Z	2 o-xylene	(Oxidized)	12 h	0	0	0	0	0
2	o-xylene +	Cu7nA115	1 h	Q /	70	42	2	40
3	1 mL iPrOH	CuZnAI-1.3	1 11	84	/8	43	3	42
4	o-xylene +	CuZnAl-1.5	1 k	70	60	(2)	4	10
4	1 mL iPrOH	(Oxidized)	1 11	12	09	03	4	10
5	o-xylene +	Cu7n 1115	10 h	100	0	0	00	00
3	1 mL iPrOH	CuZnAI-1.3	12 n	100	U	U	99	99

Table S8. STH of α-CO-PPE over various catalysts.^a

6	o-xylene +	CuZnAl-1.5	10 h	100	0	0	08	00
0	1 mL iPrOH	(Oxidized)	12 11	100	0	0	98	99
7 ^b	o-xylene	CuZnAl-1.5	12 h	0	0	0	0	0

 a Reaction conditions: 0.25 mmol α -CO-PPE, 150 mg catalyst, 3 mL solvent, 1 atm N_2, 160 °C, 12 h. b 0.25 mmol PPE.

Eatar	Cubatrata	Salvant	$C_{amy}(0/)$	Yield(%)		
Entry	Substrate	Solvent	Conv.(%)	Phenol	Acetophenone	
		o-xylene +	0	0	0	
Ι α-CO-PPE	a-CO-PPE	$200 \; \mu L \; H_2O$	0	0	0	
r	o-xylene +		0	0		
2 Gu	Gualacol	$200 \ \mu L \ H_2O$	0	0	-	
3 ^b	Guaiacol	o-xylene	0	0	-	

Table S9. Exploration of the role of water.^a

 a Conditions: 0.25 mmol substrate, 150 mg CuZnAl-1.5 (o-xylene), 3 mL solvent, 1atm $N_2,\,160$ °C, 12 h. b 150 mg CuZnAl-1.5 (water).

6. GC-MS analysis of lignin oil.

(1) GC results of lignin oil







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