Supporting Information

Reduction of CuO into Cu with guaiacol as a model compound of lignin with a homogeneous catalyst of NaOH

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Table S1. Carbon distribution in aqueous solution

Entry	Time (h)	Carbon distribution								
		IC[b]	TOC[b]	Guaiacol[a]	Catechol[a]	Fumaric[a]	Maleic[a]	Acetic[a]	Formic[a]	Oligomers[b]
1	2	4.73	85.46	67.20	8.57	0.51	1.13	0.81	0.45	5.89
	4	6.1	85.87	57.07	10.73	0.74	1.19	1.08	0.56	11.34
	6	6.42	86.29	56.73	13.17	0.93	1.34	1.12	0.50	11.35
	8	6.98	84.66	51.85	16.06	0.34	1.30	1.37	0.55	9.39
2	2	3.62	90.11	87.41	0.00	0.00	0.11	0.33	0.20	4.09
	4	7.17	87.06	61.48	1.27	1.21	1.62	1.63	0.52	6.89
	6	9.55	84.65	43.21	9.02	1.94	1.91	1.71	0.60	7.91
	8	18.30	80.35	13.73	25.71	1.10	2.26	2.41	0.83	8.88

[a]The percent of carbon in the products divided by the initial amount of carbon in guaiacol. Quantified by HPLC[a] and TOC[b] (3.75 mmol guaiacol (Entry 1)/2.65 mmol guaiacol (Entry 2), 1.0 mol/L NaOH, at 250 °C).

An energy assessment for reduction of CuO into Cu with guaiacol

For energy consumption, we added the thermodynamic calculations of reaction enthalpy (ΔH_r), Gibbs free energy (ΔG_r) and equilibrium constant (K) by using available thermodynamic database (HSC Chemistry 6 from Outokumpu Research Oy, Finland) based on Equation S(1) – S(5).

Chemical reaction: $\mathrm{aA} + \mathrm{bB} + \cdots = \mathrm{cC} + \mathrm{dD} + \cdots$ (1)

Enthalpy of reaction:

$$\Delta \mathrm{Hr} = \sum \nu \mathrm{iHi(Products)} - \sum \nu \mathrm{iHi(Reactants)} = (\mathrm{c} \cdot \mathrm{H_C} + \mathrm{d} \cdot \mathrm{H_D} + \cdots) - (\mathrm{a} \cdot \mathrm{H_A} + \mathrm{b} \cdot \mathrm{H_B} + \cdots) \quad (2)$$

Entropy of reaction:

$$\Delta \mathrm{Sr} = \sum \nu \mathrm{iSi(Products)} - \sum \nu \mathrm{iSi(Reactants)} = (\mathrm{c} \cdot \mathrm{S_C} + \mathrm{d} \cdot \mathrm{S_D} + \cdots) - (\mathrm{a} \cdot \mathrm{S_A} + \mathrm{b} \cdot \mathrm{S_B} + \cdots) \quad (3)$$

Gibbs energy of reaction:

$$\Delta \mathrm{Gr} = \sum \nu \mathrm{iGi(Procucts)} - \sum \nu \mathrm{iGi(Reactants)} = (\mathrm{c} \cdot \mathrm{G_C} + \mathrm{d} \cdot \mathrm{G_D} + \cdots) - (\mathrm{a} \cdot \mathrm{G_A} + \mathrm{b} \cdot \mathrm{G_B} + \cdots) \quad (4)$$

Equilibrium constant: $\mathrm{lgK} = \Delta \mathrm{Gr}/(-2.303 \mathrm{RT})$ (5)

where the following abbreviations have been used:

a: stoichimetric coefficient of species A in reaction

ν: stoichimetric coefficient of a species in reaction (a, b, c,…)

R: gas constant = $8.314\ \mathrm{J/(mol \cdot K)}$

T: Temperature in K

According to the reaction pathway, the main reactions were listed as Reaction (6) – (10). The hydrolysis of guaiacol is written as Reaction (6). The reaction of CuO and catechol to produce Cu with the formation of maleic, fumaric, acetic and formic acid can be written as Reaction (7) – (10), respectively.

$C_7H_8O_2$ (guaiacol) + H_2O ↔ $C_6H_6O_2$ (catechol) + CH_3OH (6)

CuO + 1/7 $C_6H_6O_2$ (catechol) → Cu + 1/7 $C_4H_4O_4$ (maleic) + 2/7 CO_2 + 1/7 H_2O (7)

$CuO + 1/7\ C_6H_6O_2$ (catechol) → $Cu + 1/7\ C_4H_4O_4$ (fumaric) + $2/7\ CO_2 + 1/7\ H_2O$ (8)

$CuO + 1/9\ C_6H_6O_2$ (catechol) → $Cu + 1/9\ C_2H_4O_2$ (acetic) + $4/9\ CO_2 + 1/9\ H_2O$ (9)

$CuO + 1/12\ C_6H_6O_2$ (catechol) → $Cu + 1/12\ CH_2O_2$ (formic) + $5/12\ CO_2 + 1/6\ H_2O$ (10)

Thermodynamic parameters of methanol and formic acid referred to the research of Khasanshin[1] and Stout[2], respectively, because their thermodynamic parameters are not available in HSC Chemistry 6. The calculated results (from 298.15 to 523.15 K) were list out according to the reaction as follows:

Table S2. Calculated thermodynamic parameters of Reaction (6).

C7H8O2(GUAg)+H2O = C6H6O2(CAT)+CH4O(l)					
T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	**kJ**	**J/K**	**kJ**		
298.150	-58.012	-188.340	-1.859	2.117E+000	0.326
373.150	-57.702	-187.354	12.209	1.954E-002	-1.709
448.150	-57.784	-187.561	26.271	8.663E-004	-3.062
523.150	-57.235	-186.456	40.309	9.440E-005	-4.025

Table S3. Calculated thermodynamic parameters of Reaction (7).

CuO + 1/7C6H6O2(CAT) = Cu + 1/7C4H4O4(MAA)+2/7CO2(g) + 1/7H2O					
T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	**kJ**	**J/K**	**kJ**		
298.150	-62.713	63.337	-81.597	1.980E+014	14.297
373.150	-62.519	63.926	-86.373	1.235E+012	12.092
448.150	-62.409	64.196	-91.178	4.249E+010	10.628
523.150	-62.289	64.442	-96.001	3.857E+009	9.586

Table S4. Calculated thermodynamic parameters of Reaction (8).

CuO + 1/7C6H6O2(CAT) = Cu + 1/7C4H4O4(E2B)+2/7CO2(g) + 1/7H2O					
T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	**kJ**	**J/K**	**kJ**		
298.150	-63.531	63.337	-82.415	2.754E+014	14.440
373.150	-63.337	63.926	-87.191	1.608E+012	12.206
448.150	-63.227	64.196	-91.996	5.292E+010	10.724
523.150	-63.107	64.442	-96.820	4.655E+009	9.668

Table S5. Calculated thermodynamic parameters of Reaction (9).

CuO + 1/9C6H6O2(CAT) = Cu + 1/9C2H4O2(ACAl)+4/9CO2(g) + 1/9H2O					
T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	**kJ**	**J/K**	**kJ**		
298.150	-65.262	94.125	-93.325	2.247E+016	16.352
373.150	-64.921	95.151	-100.427	1.146E+014	14.059
448.150	-64.634	95.853	-107.590	3.478E+012	12.541
523.150	-64.321	96.497	-114.803	2.908E+011	11.464

Table S6. Calculated thermodynamic parameters of Reaction (10).

CuO + 1/12C6H6O2(CAT) = Cu + 1/12CH2O2(l)+5/12CO2(g) + 1/6H2O					
T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	**kJ**	**J/K**	**kJ**		
298.150	-61.691	89.507	-88.378	3.053E+015	15.485
373.150	-61.241	90.860	-95.146	2.089E+013	13.320
448.150	-60.850	91.815	-101.997	7.751E+011	11.889
523.150	-60.376	92.789	-108.918	7.517E+010	10.876

The results showed that the ΔHr were negative values and the constant K decreased with the increase of temperature. Therefore, the reduction of CuO into Cu with guaiacol is an exothermic reaction.

References

(1) Khasanshin, T.; Zykova, T., Specific heat of saturated monatomic alcohols. *Journal of engineering physics* **1989,** 56, (6), 698-700.

(2) Stout, J.; Fisher, L. H., The entropy of formic acid. The heat capacity from 15 to 300 K. Heats of fusion and vaporization. *The Journal of Chemical Physics* **2004,** 9, (2), 163-168.