Supporting Information

Cu/CuMgAlO$_x$ Catalyzed Guaiacol Hydrodeoxygenation in Supercritical Methanol: A Modeling Mechanistic Insight for Lignin-derivatives Upgrading

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Fig. S1. Assembled batch reactor

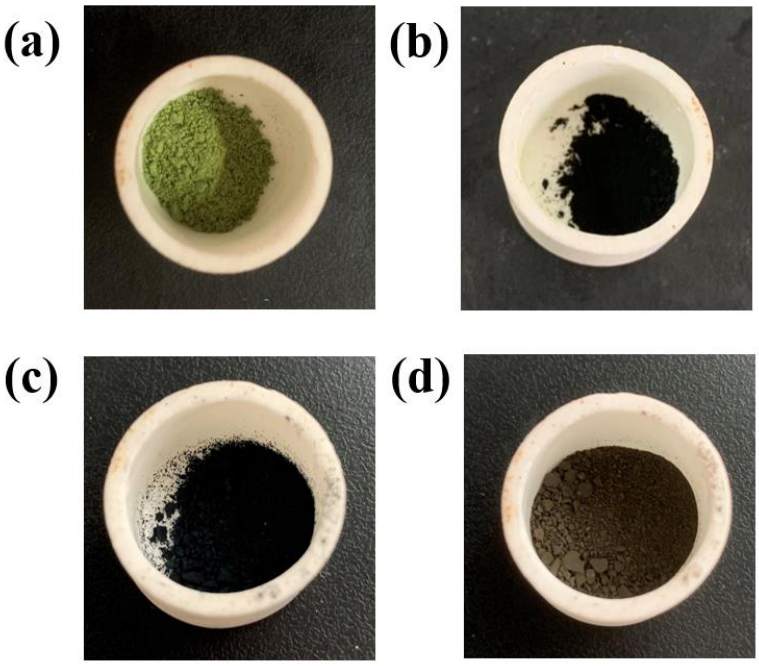

Fig. S2. Appearance of the catalysts after (a) calcination, (b) reduction, (c) reaction, and (d) recalcination.

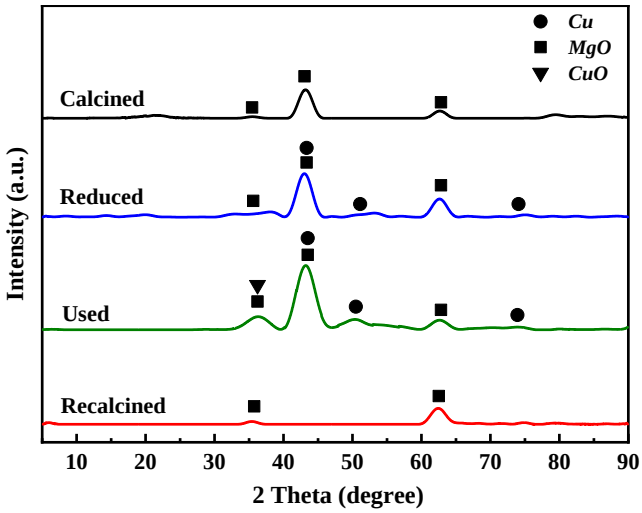

Fig. S3. XRD spectra of the catalysts after calcination, reduction, reaction, and recalcination.

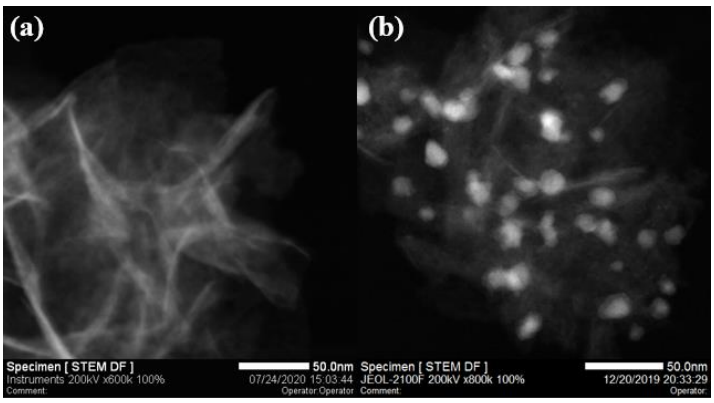

Fig. S4. STEM spectra of the catalysts after (a) calcination and (b) reduction.

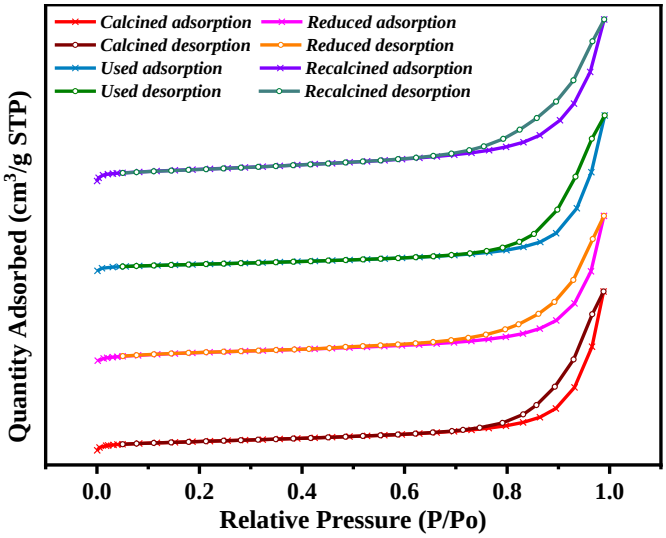

Fig. S5. N_2 absorption-desorption isotherms of the catalysts after calcination, reduction, reaction, and recalcination.

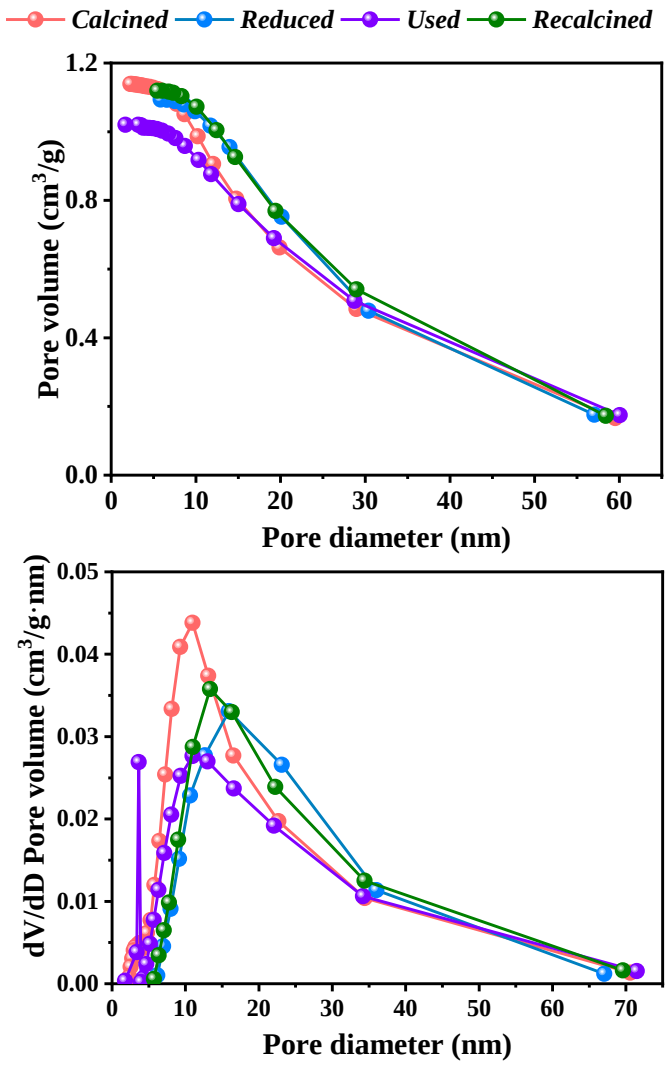

Fig. S6. BJH desorption pore size distributions of the catalysts after calcination, reduction, reaction, and recalcination.

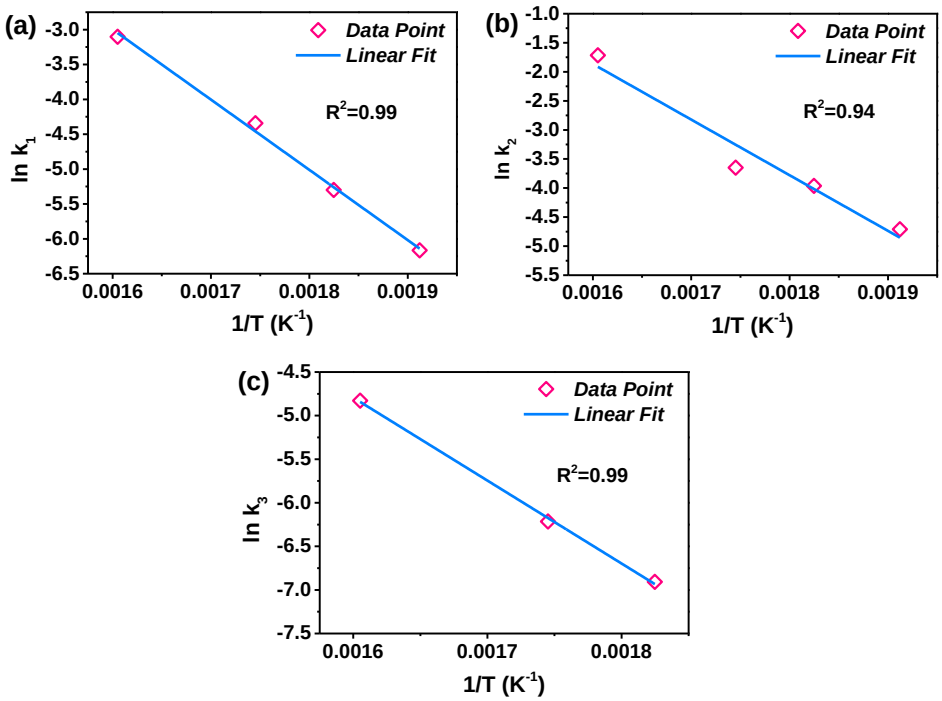

Fig. S7. The fitting results for calculating the apparent activating energies. (a) $\ln k_1$-1/T, (b) $\ln k_2$-1/T, (c) $\ln k_3$-1/T.

Table S1. Surface areas and pore analysis of the catalysts after calcination, reduction, reaction, and recalcination.

Sample	BET surface area (m^2/g)	Pore volume[a] (cm^2/g)	Pore size[b] (nm)
Calcined catalyst	237.73	1.1359	17.807
Reduced catalyst	154.84	1.0927	29.883
Used catalyst	185.23	1.0196	22.223
Regenerated catalyst	189.96	1.1176	22.048

[a]Single point adsorption total pore volume of pores.
[b]BJH desorption average pore diameter.

Table S2. Identified liquid products at 250 °C as a function of reaction time for guaiacol HDO from GC-FID[a].

Product	Yield (mol%)				
	1 min	15 min	30 min	60 min	120 min
Phenolics					
Phenol	0.00 (0.00)	0.19 (0.01)	0.39 (0.03)	1.90 (0.34)	4.95 (0.04)
2-Methyl phenol	0.00 (0.00)	0.11 (0.01)	0.10 (0.01)	0.08 (0.00)	0.27 (0.02)
3-Methyl guaiacol	0.00 (0.00)	0.05 (0.01)	0.05 (0.00)	0.01 (0.00)	0.02 (0.00)
4-Methyl guaiacol	0.00 (0.00)	0.07 (0.00)	0.12 (0.01)	0.06 (0.00)	0.46 (0.02)
5-Methyl guaiacol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.04 (0.00)
6-Methyl guaiacol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.21 (0.01)	0.00 (0.00)
Total	0.00 (0.00)	0.42 (0.02)	0.66 (0.03)	2.28 (0.34)	5.74 (0.05)
Monoalcohols					
Cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.06 (0.01)	0.26 (0.05)
2-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.05 (0.00)
3-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
2,3-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
2,5-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
2,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
3,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Methylol cyclopentane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.04 (0.01)
2-Methyl cyclopentanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.07 (0.01)	0.35 (0.05)
Diols					
1,2-Cyclohexanediol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.61 (0.16)	2.66 (0.11)
3-Methyl-1,2-cyclohexanediol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.04 (0.00)	0.16 (0.08)
Total	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.65 (0.16)	2.82 (0.14)
Ketones					
Cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)
2-Hydroxy cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.05 (0.00)

2-Methyl cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.07 (0.00)
Ethers					
Anisole	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.06 (0.01)	0.15 (0.01)
Veratrole	0.10 (0.00)	0.58 (0.06)	0.82 (0.06)	1.35 (0.11)	2.32 (0.08)
Cyclohexyl methyl ether	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
4-Methyl veratrole	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.10 (0.00)	0.58 (0.06)	0.82 (0.06)	1.43 (0.11)	2.47 (0.08)
Cycloalkanes					
Cyclohexane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
1-Methyl cyclohexane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Methyl cyclopentane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Others					
Benzene	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Totals					
Conversion of guaiacol	0.50 (0.12)	8.06 (0.24)	16.51 (0.21)	21.80 (0.61)	32.76 (0.62)
Total yields of OUPs	0.10 (0.00)	1.00 (0.06)	1.48 (0.07)	3.69 (0.36)	8.21 (0.09)
Total yields of OSPs	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.72 (0.16)	3.24 (0.15)
Total yields of cycloalkanes	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total yields of monomers	0.10 (0.00)	1.00 (0.06)	1.48 (0.07)	4.41 (0.39)	11.45 (0.17)
Unknown[b]	0.40 (0.12)	7.06 (0.25)	15.03 (0.22)	17.39 (0.73)	21.31 (0.64)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of $Cu/CuMgAlO_x$, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Standard errors were shown in parentheses. [b]Defined as the difference between the guaiacol conversion and total yields of identified products.

Table S3. Identified liquid products at 275 °C as a function of reaction time for guaiacol HDO from GC-FID[a].

Product	Yield (mol%)				
	1 min	15 min	30 min	60 min	120 min
Phenolics					
Phenol	0.10 (0.00)	0.19 (0.15)	0.40 (0.85)	1.68 (0.12)	11.03 (1.23)
2-Methyl phenol	0.00 (0.00)	0.05 (0.00)	0.06 (0.01)	0.08 (0.01)	0.00 (0.00)
3-Methyl guaiacol	0.00 (0.00)	0.03 (0.01)	0.03 (0.00)	0.12 (0.01)	0.34 (0.12)
4-Methyl guaiacol	0.00 (0.00)	0.02 (0.02)	0.03 (0.12)	0.33 (0.05)	0.89 (0.16)
5-Methyl guaiacol	0.00 (0.00)	0.02 (0.01)	0.08 (0.25)	0.00 (0.00)	0.00 (0.00)
6-Methyl guaiacol	0.00 (0.00)	0.04 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.10 (0.00)	0.35 (0.15)	0.60 (0.89)	2.21 (0.13)	12.26 (1.25)
Monoalcohols					
Cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.09 (0.20)	3.36 (1.28)
2-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.05)	0.85 (0.33)
3-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.10 (0.01)
2,3-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.37 (0.00)
2,5-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
2,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.24 (0.00)
3,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.16 (0.12)
Methylol cyclopentane	0.00 (0.00)	0.00 (0.00)	0.07 (0.02)	0.02 (0.03)	0.77 (0.04)
2-Methyl cyclopentanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.00 (0.00)	0.00 (0.00)	0.07 (0.02)	0.15 (0.21)	5.85 (1.33)
Diols					
1,2-Cyclohexanediol	0.10 (0.01)	0.00 (0.00)	0.00 (0.00)	0.67 (0.36)	12.96 (1.10)
3-Methyl-1,2-cyclohexanediol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.06 (0.04)	0.87 (0.25)
Total	0.10 (0.01)	0.00 (0.00)	0.00 (0.00)	0.73 (0.36)	13.83 (1.13)
Ketones					
Cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.12 (0.54)
2-Hydroxy cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)

2-Methyl cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.28 (0.01)
Total	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.40 (0.54)
Ethers					
Anisole	0.00 (0.00)	0.00 (0.00)	0.01 (0.01)	0.08 (0.01)	0.85 (0.01)
Veratrole	0.10 (0.00)	0.38 (0.14)	0.63 (0.23)	1.64 (0.01)	3.53 (0.28)
Cyclohexyl methyl ether	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
4-Methyl veratrole	0.00 (0.00)	0.05 (0.00)	0.00 (0.00)	0.00 (0.00)	0.11 (0.01)
Total	0.10 (0.00)	0.43 (0.14)	0.64 (0.23)	1.72 (0.01)	4.49 (0.28)
Cycloalkanes					
Cyclohexane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.55 (0.01)
1-Methyl cyclohexane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Methyl cyclopentane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.55 (0.01)
Others					
Benzene	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.01 (0.02)
Totals					
Conversion of guaiacol	1.21 (0.12)	8.90 (0.22)	19.30 (0.32)	29.20 (0.35)	75.00 (2.35)
Total yields of OUPs	0.20 (0.00)	0.78 (0.21)	1.24 (0.92)	3.94 (0.13)	16.76 (1.28)
Total yields of OSPs	0.10 (0.01)	0.00 (0.00)	0.07 (0.02)	0.88 (0.42)	20.08 (1.82)
Total yields of cycloalkanes	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.55 (0.01)
Total yields of monomers	0.30 (0.01)	0.78 (0.21)	1.31 (0.92)	4.82 (0.44)	37.39 (2.23)
Unknown[b]	0.91 (0.12)	8.12 (0.30)	17.99 (0.98)	24.38 (0.56)	37.61 (3.24)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of Cu/CuMgAlO_x, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Standard errors were shown in parentheses. [b]Defined as the difference between the guaiacol conversion and total yields of identified products.

Table S4. Identified liquid products at 300 °C as a function of reaction time for guaiacol HDO from GC-FID[a].

Product	Yield (mol%)				
	1 min	15 min	30 min	60 min	120 min
Phenolics					
Phenol	0.10 (0.00)	0.81 (0.17)	2.52 (0.96)	5.61 (0.14)	4.00 (1.13)
2-Methyl phenol	0.00 (0.00)	0.10 (0.00)	0.13 (0.01)	0.13 (0.01)	0.00 (0.00)
3-Methyl guaiacol	0.00 (0.00)	0.12 (0.00)	0.04 (0.00)	1.10 (0.01)	0.00 (0.00)
4-Methyl guaiacol	0.00 (0.00)	0.03 (0.00)	0.65 (0.32)	1.04 (0.02)	2.33 (0.24)
5-Methyl guaiacol	0.00 (0.00)	0.34 (0.01)	0.94 (0.24)	0.02 (0.00)	0.00 (0.00)
6-Methyl guaiacol	0.00 (0.00)	0.04 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.10 (0.00)	1.44 (0.17)	4.28 (1.04)	7.90 (0.14)	6.33 (1.16)
Monoalcohols					
Cyclohexanol	0.00 (0.00)	0.02 (0.00)	0.27 (0.21)	1.06 (0.22)	23.41 (2.36)
2-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.08 (0.07)	0.31 (0.07)	7.14 (0.31)
3-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.03 (0.00)	1.14 (0.06)
2,3-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.02 (0.02)	0.37 (0.00)
2,5-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.00 (0.00)	0.06 (0.00)
2,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.05 (0.00)
3,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.16 (0.01)
Methylol cyclopentane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.46 (0.09)	4.12 (0.04)
2-Methyl cyclopentanol	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.05 (0.01)	0.27 (0.03)
Total	0.00 (0.00)	0.02 (0.00)	0.37 (0.22)	1.96 (0.25)	36.72 (2.38)
Diols					
1,2-Cyclohexanediol	0.10 (0.01)	0.34 (0.08)	1.92 (0.89)	19.43 (0.40)	8.68 (0.10)
3-Methyl-1,2-cyclohexanediol	0.00 (0.00)	0.00 (0.00)	0.16 (0.09)	0.31 (0.06)	4.54 (0.28)
Total	0.10 (0.01)	0.34 (0.08)	2.08 (0.89)	19.74 (0.40)	13.22 (0.30)
Ketones					
Cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.11 (0.01)	0.54 (0.54)
2-Hydroxy cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.04 (0.01)	0.01 (0.00)	0.00 (0.00)

2-Methyl cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.28 (0.01)
Total	0.00 (0.00)	0.00 (0.00)	0.05 (0.01)	0.13 (0.01)	0.82 (0.54)
Ethers					
Anisole	0.00 (0.00)	0.02 (0.00)	0.09 (0.05)	0.28 (0.04)	2.17 (0.01)
Veratrole	0.50 (0.10)	1.54 (0.14)	2.93 (0.53)	3.83 (0.00)	5.63 (0.13)
Cyclohexyl methyl ether	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.04 (0.01)	0.20 (0.01)
4-Methyl veratrole	0.00 (0.00)	0.05 (0.00)	0.00 (0.00)	0.03 (0.00)	0.09 (0.00)
Total	0.50 (0.10)	1.61 (0.14)	3.02 (0.53)	4.18 (0.04)	8.09 (0.13)
Cycloalkanes					
Cyclohexane	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.06 (0.02)	2.99 (0.27)
1-Methyl cyclohexane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.44 (0.00)
Methyl cyclopentane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.01 (0.00)	0.03 (0.00)
Total	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.09 (0.02)	3.46 (0.27)
Others					
Benzene	0.00 (0.00)	0.01 (0.00)	0.10 (0.02)	0.06 (0.01)	0.01 (0.02)
Totals					
Conversion of guaiacol	3.40 (0.35)	14.40 (0.19)	31.10 (0.59)	57.75 (0.62)	97.00 (0.20)
Total yields of OUPs	0.60 (0.10)	3.06 (0.22)	7.40 (1.17)	12.10 (0.15)	14.23 (1.16)
Total yields of OSPs	0.10 (0.01)	0.36 (0.08)	2.50 (0.92)	21.87 (0.48)	50.96 (2.46)
Total yields of cycloalkanes	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.09 (0.02)	3.46 (0.27)
Total yields of monomers	0.70 (0.10)	3.42 (0.23)	9.92 (1.49)	34.06 (0.50)	68.65 (2.73)
Unknown[b]	2.70 (0.36)	10.98 (0.30)	21.18 (1.60)	23.69 (0.80)	28.35 (2.74)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of Cu/CuMgAlO_x, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Standard errors were shown in parentheses. [b]Defined as the difference between the guaiacol conversion and total yields of identified products.

Table S5. Identified liquid products at 350 °C as a function of reaction time for guaiacol HDO from GC-FID[a].

Product	Yield (mol%)				
	1 min	15 min	30 min	60 min	120 min
Phenolics					
Phenol	0.30 (0.01)	3.52 (0.33)	6.59 (0.51)	0.00 (0.00)	0.00 (0.00)
2-Methyl phenol	0.00 (0.00)	0.09 (0.00)	0.29 (0.01)	0.00 (0.00)	0.00 (0.00)
3-Methyl guaiacol	0.01 (0.00)	0.02 (0.00)	0.67 (0.00)	0.00 (0.00)	0.00 (0.00)
4-Methyl guaiacol	0.00 (0.00)	0.03 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
5-Methyl guaiacol	0.00 (0.00)	0.01 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
6-Methyl guaiacol	0.00 (0.00)	1.29 (0.08)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Total	0.40 (0.01)	4.96 (0.34)	7.55 (0.51)	0.00 (0.00)	0.00 (0.00)
Monoalcohols					
Cyclohexanol	0.00 (0.00)	0.42 (0.03)	22.04 (1.92)	12.33 (0.61)	2.08 (0.27)
2-Methyl cyclohexanol	0.00 (0.00)	0.10 (0.00)	8.58 (0.20)	25.11 (1.60)	13.05 (0.02)
3-Methyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	1.36 (0.12)	1.06 (0.01)	0.51 (0.03)
2,3-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.37 (0.00)	1.96 (0.15)	1.62 (0.01)
2,5-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.13 (0.01)	2.48 (0.27)	2.68 (0.09)
2,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	0.33 (0.03)	0.36 (0.02)	0.19 (0.01)
3,6-Dimethyl cyclohexanol	0.00 (0.00)	0.00 (0.00)	1.92 (0.05)	0.03 (0.00)	2.56 (0.05)
Methylol cyclopentane	0.00 (0.00)	0.18 (0.00)	0.04 (0.00)	0.08 (0.00)	0.11 (0.00)
2-Methyl cyclopentanol	0.00 (0.00)	0.00 (0.00)	0.42 (0.01)	1.12 (0.25)	1.54 (0.01)
Total	0.00 (0.00)	0.70 (0.03)	35.19 (1.94)	44.53 (1.76)	24.34 (0.29)
Diols					
1,2-Cyclohexanediol	0.10 (0.01)	2.23 (0.42)	17.68 (0.35)	0.00 (0.00)	0.00 (0.00)
3-Methyl-1,2-cyclohexanediol	0.00 (0.00)	0.18 (0.01)	1.78 (0.06)	0.00 (0.00)	0.00 (0.00)
Total	0.10 (0.01)	2.41 (0.42)	19.46 (0.36)	0.00 (0.00)	0.00 (0.00)
Ketones					
Cyclohexanone	0.00 (0.00)	0.05 (0.00)	0.88 (0.03)	0.45 (0.02)	0.00 (0.00)
2-Hydroxy cyclohexanone	0.00 (0.00)	0.10 (0.00)	0.14 (0.01)	0.20 (0.02)	0.15 (0.01)

2-Methyl cyclohexanone	0.00 (0.00)	0.00 (0.00)	0.08 (0.00)	0.25 (0.02)	0.28 (0.01)
Total	0.00 (0.00)	0.15 (0.00)	1.10 (0.03)	0.90 (0.03)	0.43 (0.01)
Ethers					
Anisole	0.01 (0.00)	0.13 (0.01)	2.21 (0.11)	2.80 (0.11)	1.40 (0.02)
Veratrole	0.90 (0.05)	2.56 (0.06)	3.67 (0.23)	0.31 (0.06)	0.00 (0.00)
Cyclohexyl methyl ether	0.00 (0.00)	0.00 (0.00)	0.17 (0.00)	1.25 (0.12)	2.00 (0.03)
4-Methyl veratrole	0.00 (0.00)	0.00 (0.00)	0.90 (0.01)	0.00 (0.00)	0.00 (0.00)
Total	0.91 (0.05)	2.69 (0.06)	6.95 (0.26)	4.36 (0.17)	3.40 (0.04)
Cycloalkanes					
Cyclohexane	0.00 (0.00)	0.04 (0.00)	5.24 (0.15)	13.93 (1.45)	18.38 (0.35)
1-Methyl cyclohexane	0.00 (0.00)	0.03 (0.01)	0.46 (0.02)	3.27 (0.50)	8.48 (0.05)
Methyl cyclopentane	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
1, 3-Dimethyl cyclohexane	0.00 (0.00)	0.02 (0.00)	0.07 (0.01)	0.00 (0.00)	2.57 (0.04)
1, 4-Dimethyl cyclohexane	0.00 (0.00)	0.00 (0.00)	0.03 (0.00)	0.28 (0.05)	1.36 (0.01)
Total	0.00 (0.00)	0.09 (0.01)	5.80 (0.15)	17.48 (1.53)	30.79 (0.36)
Others					
Benzene	0.01 (0.00)	0.00 (0.00)	0.24 (0.02)	1.36 (0.18)	1.47 (0.10)
Totals					
Conversion of guaiacol	9.01 (0.35)	34.01 (2.14)	92.75 (2.66)	99.58 (0.11)	99.81 (0.01)
Total yields of OUPs	1.32 (0.05)	7.65 (0.34)	14.57 (0.57)	4.47 (0.22)	2.87 (0.10)
Total yields of OSPs	0.10 (0.01)	3.26 (0.42)	55.92 (1.97)	46.68 (1.76)	26.77 (0.29)
Total yields of cycloalkanes	0.00 (0.00)	0.09 (0.01)	5.80 (0.15)	17.48 (1.53)	30.79 (0.36)
Total yields of monomers	1.42 (0.05)	11.00 (0.54)	76.29 (2.05)	68.63 (2.35)	60.43 (0.47)
Unknown[b]	7.59 (0.35)	23.01 (2.21)	16.46 (3.36)	30.95 (2.35)	39.38 (0.47)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of Cu/CuMgAlO_x, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Standard errors were shown in parentheses. [b]Defined as the difference between the guaiacol conversion and total yields of the products.

Table S6. Gaseous products at 250 °C as a function of reaction time for guaiacol HDO from GC-TCD[a].

Yields (mol%)	Reaction time				
	1 min	15 min	30 min	60 min	120 min
CH_4	N/A[b]	N/A	0.01 (0.00)	0.03 (0.01)	0.10 (0.01)
CO	N/A	N/A	0.02 (0.00)	0.22 (0.04)	0.70 (0.01)
CO_2	N/A	N/A	0.03 (0.00)	0.13 (0.00)	0.21 (0.02)
Total	N/A	N/A	0.06 (0.00)	0.38 (0.05)	1.01 (0.00)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of $Cu/CuMgAlO_x$, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Values in parentheses represented the standard error.
[b]N/A: not applicable.

Table S7. Gaseous products at 275 °C as a function of reaction time for guaiacol HDO from GC-TCD[a].

Yields (mol%)	Reaction time				
	1 min	15 min	30 min	60 min	120 min
CH_4	N/A[b]	N/A	0.01 (0.00)	0.06 (0.00)	0.35 (0.03)
CO	N/A	N/A	0.03 (0.00)	0.41 (0.01)	2.50 (0.00)
CO_2	N/A	N/A	0.03 (0.00)	0.14 (0.01)	0.30 (0.01)
Total	N/A	N/A	0.07 (0.00)	0.61 (0.02)	3.15 (0.00)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of $Cu/CuMgAlO_x$, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Values in parentheses represented the standard error.
[b]N/A: not applicable.

Table S8. Gaseous products at 300 °C as a function of reaction time for guaiacol HDO from GC-TCD[a].

Yields (mol%)	Reaction time				
	1 min	15 min	30 min	60 min	120 min
CH_4	N/A[b]	0.02 (0.00)	0.12 (0.02)	0.21 (0.02)	0.90 (0.03)
CO	N/A	0.16 (0.01)	0.86 (0.17)	1.44 (0.14)	3.89 (0.15)
CO_2	N/A	0.08 (0.01)	0.26 (0.04)	0.25 (0.02)	0.63 (0.02)
Total	N/A	0.26 (0.02)	1.24(0.23)	1.90 (0.19)	5.42 (0.19)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of Cu/CuMgAlO_x, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Values in parentheses represented the standard error.
[b]N/A: not applicable.

Table S9. Gaseous products at 350 °C as a function of reaction time for guaiacol HDO from GC-TCD[a].

Yields (mol%)	Reaction time				
	1 min	15 min	30 min	60 min	120 min
CH_4	N/A[b]	0.13 (0.00)	0.93 (0.09)	3.30 (0.07)	8.20 (0.01)
CO	N/A	1.25 (0.06)	7.02 (0.08)	7.60 (0.04)	8.80 (0.05)
CO_2	N/A	0.17 (0.01)	0.61 (0.05)	1.05 (0.01)	1.95 (0.01)
Total	N/A	1.55 (0.07)	8.56 (0.06)	11.95 (0.04)	18.95 (0.03)

[a]Reaction conditions: 100 mg of guaiacol, 100 mg of Cu/CuMgAlO_x, 2.4 g of MeOH with dodecane as the internal standard. Each reaction was run in duplicate/triplicate. Values in parentheses represented the standard error.
[b]N/A: not applicable.