

Supplementary Information

Table S1. Guaiacol upgrading in an aqueous environment over different catalysts ^a.

Catalyst	Guaiacol conversion (%)	Selectivity to catechol (%)	Selectivity to phenol (%)	Gravimetric mass balance ^b (%)
AC	22	44	1	96
7.5% Ac/AC	36	34	5	93
20% Ac/AC	N.M.	N.M.	N.M.	N.M.
7.5% Am/AC	47	34	6	92
20% Am/AC	63	25	4	77
CNF	31	27	1	98
7.5% Ac/CNF	31	39	2	99
20% Ac/CNF	29	47	3	99
7.5% Am/CNF	25	49	4	99
20% Am/CNF	24	54	7	96
CNT	54	29	2	92
7.5% Ac/CNT	51	18	1	74
20% Ac/CNT	41	17	0	91
7.5% Am/CNT	44	15	1	86
20% Am/CNT	58	12	1	81

^a Reaction conditions: 0.125 g catalyst, 1.25 g guaiacol, 11.25 g water, 300 °C, 2000 psi of H₂, 4 h.

^b Gravimetric mass balance = $100 \times (\text{mass of starting reaction mixture})/(\text{mass of recovered liquids and solids})$. N.M.: not measured.

Table S2. Product distribution of guaiacol upgrading experiments performed in dodecane over different catalysts ^a.

Catalyst	Unconverted guaiacol (mg)	Cyclohexane (mg)	Cyclohexanone (mg)	Cyclohexanol (mg)	2-methoxy cyclohexanol (mg)	Cyclohexanediol (mg)	Phenol (mg)	Catechol (mg)	Coke (mg) ^b
None	1166	1	0	0	0	0	0	19	0
AC	1109	1	0	3	<1	1	5	21	155
7.5% Ac/AC	943	2	0	4	1	7	40	69	N/A
20% Ac/AC	493	3	0	4	1	7	69	52	45
7.5% Am/AC	794	26	0	5	16	4	5	95	N/A
20% Am/AC	583	9	0	4	1	1	17	203	N/A
CNF	1187	0	0	2	0	0	2	19	N/A
7.5% Ac/CNF	754	0	0	3	1	5	61	53	5
20% Ac/CNF	558	0	0	0	0	5	246	85	N/A
7.5% Am/CNF	841	0	0	3	0	7	161	55	N/A
20% Am/CNF	589	0	0	6	0	5	245	104	5
CNT	1056	1	0	3	<1	1	4	31	205
7.5% Ac/CNT	351	0	0	2	0	2	25	322	315
20% Ac/CNT	119	82	0	4	7	9	57	280	305
7.5% Am/CNT	855	0	0	3	0	2	14	188	N/A
20% Am/CNT	946	1	0	2	0	4	111	39	65

^a Reaction conditions: 0.125 g catalyst, 1.25 g guaiacol, 11.25 g dodecane, 300 °C, 580 psi of H₂, 4 h. ^b Defined as the weight of catalyst added to the reactor subtracted from the weight of recovered solids. Note: in cells marked "N/A" the aforementioned subtraction afforded a slightly negative number, which suggests that the recovery of solids was incomplete and was taken as an indication of negligible coke formation.

Table S3. Product distribution of guaiacol upgrading experiments performed in dodecane at 350 °C ^a.

Catalyst	Unconverted guaiacol (mg)	Cyclohexane (mg)	Cyclohexanone (mg)	Cyclohexanol (mg)	2-methoxy cyclohexanol (mg)	Cyclohexanediol (mg)	Phenol (mg)	Catechol (mg)	Coke (mg) ^b
None	266	1	0	2	3	4	15	47	0
7.5% Am/CNF	7	29	0	6	3	2	607	1	65
20% Am/CNF	23	13	0	6	3	1	596	1	65

^a Reaction conditions: 0.125 g catalyst, 1.25 g guaiacol, 11.25 g dodecane, 350 °C, 580 psi of H₂, 4 h.

^b Defined as the weight of catalyst added to the reactor subtracted from the weight of recovered solids.

Table S4. Molar mass balance showing weight of possible high molecular weight products ^a.

Catalyst	Unconverted guaiacol (mmol)	Cyclohexane (mmol)	Cyclohexanone (mmol)	Cyclohexanol (mmol)	2-methoxy cyclohexanol (mmol)	Cyclohexanediol (mmol)	Phenol (mmol)	Catechol (mmol)	Coke (mg) ^b	Unidentifiable and/or undetectable products (mg) ^c
None	9.392	0.011	0	0	0	0	0	0.172	0	61.10
None*	2.143	0.011	0	0.019	0.023	0.034	0.159	0.426	0	900.1
AC	8.933	0.011	0	0.029	0.007	0.008	0.053	0.190	155	113.3
7.5% Ac/AC	7.596	0.023	0	0.039	0.007	0.060	0.425	0.626	N/A	180.0
20% Ac/AC	3.971	0.035	0	0.039	0.007	0.060	0.733	0.472	45	609.4
7.5% Am/AC	6.396	0.308	0	0.049	0.122	0.034	0.053	0.862	N/A	288.2
20% Am/AC	4.696	0.106	0	0.039	0.007	0.008	0.180	1.843	N/A	395.4
CNF	9.561	0	0	0.019	0	0	0.021	0.172	N/A	46.46
7.5% Ac/CNF	6.073	0	0	0.029	0.007	0.043	0.648	0.481	5	345.7
20% Ac/CNF	4.494	0	0	0	0	0.043	2.613	0.772	N/A	286.3
7.5% Am/CNF	6.774	0	0	0.029	0	0.060	1.710	0.499	N/A	133.4
7.5% Am/CNF*	0.056	0.344	0	0.059	0.023	0.017	6.449	0.009	65	385.9
20% Am/CNF	4.744	0	0	0.059	0	0.043	2.603	0.944	5	207.7
20% Am/CNF*	0.185	0.154	0	0.059	0.023	0.008	6.333	0.009	65	419.0
CNT	8.506	0.011	0	0.029	0.007	0.008	0.042	0.281	205	156.3
7.5% Ac/CNT	2.827	0	0	0.019	0	0.017	0.265	2.924	315	498.0
20% Ac/CNT	0.958	0.974	0	0.039	0.053	0.077	0.605	2.543	305	607.5
7.5% Am/CNT	6.887	0	0	0.029	0	0.017	0.148	1.707	N/A	178.7
20% Am/CNT	7.620	0.011	0	0.019	0	0.034	1.179	0.354	65	105.3

^a Reaction conditions: 0.125 g catalyst, 0.43 g guaiacol, 0.43 g acetic acid, 0.44 g furfural, 11.25 g dodecane, 300 °C (unless otherwise indicated), 580 psi of H₂, 4 h. ^b Defined as the weight of catalyst added to the reactor subtracted from the weight of recovered solids. Note: in cells marked “N/A” the aforementioned subtraction afforded a slightly negative number, which suggests that the recovery of solids was incomplete and was taken as an indication of negligible coke formation. ^c Defined as the quantity of guaiacol which was not identified as unconverted starting material, products, or coke. If N/A appears in the coke column, coke was assumed to be zero. *Indicates reactions carried out at 350 °C.

Table S5. Sequential guaiacol upgrading runs in dodecane over 20%Am/CNF ^a.

Run	Unconverted guaiacol (mg)	Cyclohexane (mg)	Cyclohexanone (mg)	Cyclohexanol (mg)	2-methoxy cyclohexanol (mg)	Cyclohexanediol (mg)	Phenol (mg)	Catechol (mg)	Coke (mg) ^b
1	301	7	0	3	1	11	474	17	55
2	467	1	0	2	0	1	280	26	5
3	546	0	0	2	0	3	225	32	N/A

^a Reaction conditions: 300 °C, 580 psi of H₂, 4 h. Run 1: 0.125 g catalyst, 1.25 g guaiacol, 11.25 g dodecane; Run 2: 0.125 g catalyst, 1.25 g guaiacol, 11.25 g dodecane; Run 3: 0.117 g catalyst, 1.17 g guaiacol, 10.53 g dodecane. ^b Defined as the weight of catalyst added to the reactor subtracted from the weight of recovered solids. Note: in cells marked “N/A” the aforementioned subtraction afforded a slightly negative number, which suggests that the recovery of solids was incomplete and was taken as an indication of negligible coke formation.

Table S6. Product distribution of guaiacol upgrading in the presence of acetic acid and furfural ^a.

Catalyst	Unconverted guaiacol (mg)	Unconverted acetic acid (mg)	Unconverted furfural (mg)	Cyclohexanol (mg)	Phenol (mg)	Catechol (mg)	Ethyl acetate (mg)	Tetrahydrofurfuryl alcohol (mg)	γ -butyrolactone (mg)	Coke (mg) ^b
20% Am/CNF	403	139	89	1	17	6	4	1	2	165

^a Reaction conditions: 0.125 g catalyst, 0.43 g guaiacol, 0.43 g acetic acid, 0.44 g furfural, 11.25 g dodecane, 300 °C, 580 psi of H₂, 4 h. ^b Defined as the weight of catalyst added to the reactor subtracted from the weight of recovered solids.

Table S7. Calibration solution composition, retention times and response factors.

Constituent	Retention time	Response factor	Calibration solutions (g)				
			1	2	3	4	5
Cyclohexane	0.5	0.83	0.00	0.02	0.04	0.00	0.00
Ethyl acetate	0.9	0.55	0.00	0.00	0.00	0.06	0.13
Ethanol	1.0	N/A*	0.00	0.00	0.00	0.06	0.13
Cyclopentanone	3.4	1.13	0.00	0.00	0.00	0.00	0.01
Cyclohexanone	5.4	1.34	0.00	0.01	0.00	0.00	0.00
Cyclopentanol	6.2	1.11	0.00	0.00	0.00	0.03	0.05
Cyclohexanol	8.2	1.18	0.00	0.01	0.01	0.00	0.00
Acetic acid	8.6	0.36	0.00	0.00	0.00	0.50	0.19
Furfural	9.0	0.68	0.00	0.00	0.10	0.50	0.19
Tetrahydrofurfuryl alcohol	9.6	0.77	0.00	0.00	0.00	0.00	0.01
2-methoxycyclohexanol	9.8	0.92	0.00	0.01	0.01	0.00	0.00
γ -butyrolactone	11.1	1.02	0.00	0.00	0.00	0.01	0.01
1,2-pentanediol	13.1	0.73	0.00	0.00	0.00	0.00	0.01
Guaiacol	13.8	1.09	1.26	0.95	0.25	0.06	0.50
1,2-cyclohexanediols	14.5	1.10	0.00	0.01	0.01	0.00	0.00
Phenol	15.2	1.28	0.00	0.25	0.76	0.00	0.00
Levulinic acid	18.1	0.58	0.00	0.00	0.00	0.02	0.04
Catechol	20.8	0.97	0.00	0.02	0.08	0.00	0.00
Sec-butanol	1.6	Internal Standard	1.21	1.21	1.21	1.21	1.21
Chloroform		Solvent	11.25	11.25	11.25	11.25	11.25

*A response factor for ethanol could not be determined. Chloroform (stabilized with ethanol) was used as a solvent and thus interferes with the ethanol product signal.

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