Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

Mapping reactivities of aromatic models with a lignin disassembly catalyst. Steps toward controlling product selectivity.

by Christopher M. Bernt, Giovanni Bottari, Jacob A. Barrett, Susannah L. Scott, Katalin Barta, Peter C. Ford

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Analysis of GC-FID and GC-MS Data

Final concentrations of analytes in this study were derived using different approaches based on whether the data was collected via GC-MS or GC-FID. In both cases decane was used as a reference and an internal standard. Control experiments under our standard reaction conditions indicated negligible change in decane for up to 24 hours. Standard curves for decane were created for each instrument used in this study. The total amount of each compound at the end of a reaction was calculated using formula (1) which accounts for changes in solvent volumes over the course of the experiment and GC preparation.

$$nmol_{analyte} = \left(\frac{\boldsymbol{A}_{analyte}}{\boldsymbol{rf}_{analyte}}\right)\left(\frac{Decane_{theoretical}}{Decane_{measured}}\right) \qquad eq. 1$$

A is the integrated area of the peak associated with the given analyte, **rf** is the nmolar response factor (nmol/µL) of the given analyte, and the theoretical decane is the amount added at the beginning of the experiment.

When analysis was performed by GC-MS, standard curves were generated using the area of the GC-MS response for each target molecule. Unless specifically noted, these were the **rf** values used in eq. 1.

For experiments using the GC-FID the quantities of most products were calculated using the concept of effective carbon number (ECN), an approximation originally described by Sternberg et al. [1] This approximation is based on the mechanism of the FID response; this response is generally proportional to the carbon content of a given compound but can be modulated by bond structure and oxygen content.[1,2] The magnitude of the ECN is proportional to a given compounds response, and hence the ratio of ECN between two compounds directly related to the ratio of the two compounds' molar response. Rearranging equations described by Scanlon et al.[2] and applying a basic definition of a molar response factor (2) gives equation (3)

$$[Compound] = \left(\frac{\boldsymbol{A}_{compound}}{\boldsymbol{rf}_{compound}}\right) \qquad eq. 2$$

$$\boldsymbol{rf}_{analyte} = (\boldsymbol{rf}_{decane})\left(\frac{\boldsymbol{ECN}_{analyte}}{\boldsymbol{ECN}_{decane}}\right) \qquad eq. 3$$

The theoretical response factors calculated for this study are given in table 1 and based on theoretical ECN contributions provided by Sternberg and Scanlon.[1,2] This study uses these values to calculate the analyte quantities for FID experiments.

The material balance was calculated from the moles of products determined for a given time point divided by the moles of substrate present at the start of the experiment (based on GC response).

1. J.C. Sternberg, W.S. Gallaway, and D.T.L. Jones. The mechanism of response of flame ionization detectors. In ***Gas Chromatography.*** N. Brenner, J.E. Callen, and M.D. Weiss, eds. Academic Press, New York, 1962, pp. 231-67.
2. Scanlon, J. T.; Willis, D. E. Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept. *J. Chromatogr. Sci.* **1985**, *23*, 333-340

Discussion on Descriptive Statistics for Global Fitting of Kinetics Data

In this study we applied global kinetics fitting of non-linear data with several parameters to define these reaction networks, which makes formal statistical analysis a complex proposition. However, our goal is to utilize the simplest, chemically reasonable model and descriptive statistics to describe the observed product evolution and to show that the kinetics parameters obtained are self-consistent over the range of compounds studied.

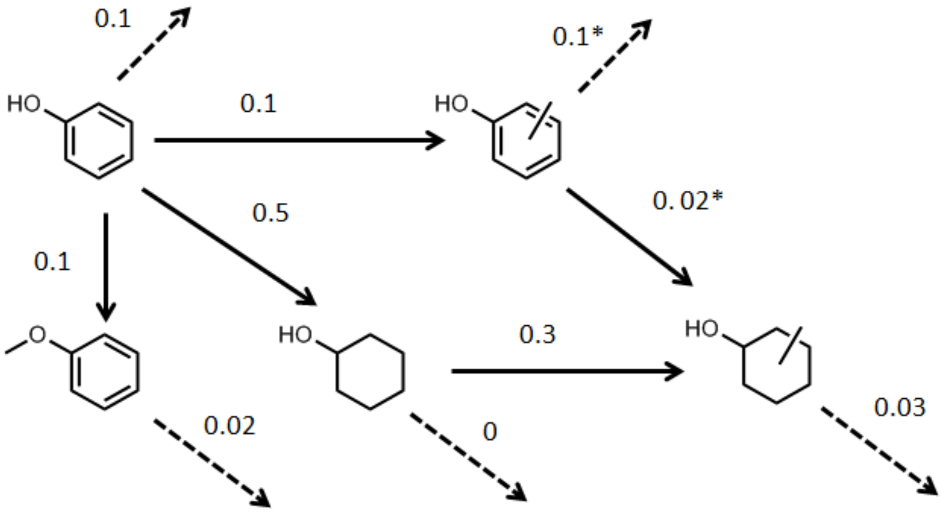
The R^2 values (coefficient of determination) of the individual fits provide insight into how much of the data is actually explained, and the lowest of these is greater than 0.85 (R^2 values for individual fits are given for individual compounds in this SI). This can be classically interpreted to mean that at least 85% of the variance in product distribution as a function of time is explained by the pseudo-first order fits. In the case of highly varied reactivities between species, this was sufficient to identify phenolics as the primary sources of product proliferation.

In looking at consistency across studies, we can compare the rate constants and standard error (typically 20% or less) as determined by global fitting. In the case of reaction networks that share a reaction pathway (e.g. hydrogenation of phenol, starting with either phenol as a substrate or as a product of the guaiacol pathway) the values were indistinguishable within the experimental uncertainties. The parallel observation also held: pathways identified in as being significantly different in this study varied from each other in a magnitude greater than the individual errors. These results argue against major interferences of the catalytic rates of, or products from, specific substrates from the presence of other characteristic substrates among the systems studied.

Table S-0. Theoretical response factors and ECN calculated for FID experiments.

Compound	**Calc. r.f.**	**F (R-Molar)**	**ECN**	aliphatic carbons	aromatic carbons	olefinic carbons	carbonyl carbons	ether oxygens	1° alcohol oxygens	2° alcohol oxygens
***Decane (Standard)**	**26339**	**1.00**	**10.00**	**10**	**0**	**0**	**0**	**0**	**0**	**0**
cyclohexane	15803	1.67	6.00	6	0	0	0	0	0	0
cyclohexanediol	11852	2.22	4.50	6	0	0	0	0	0	2
cyclohexanol	13828	1.90	5.25	6	0	0	0	0	0	1
cyclohexanone	13169	2.00	5.00	5	0	0	1	0	0	0
cyclohexene	15540	1.69	5.90	4	0	2	0	0	0	0
cyclohexylmethanol	17120	1.54	6.50	7	0	0	0	0	1	0
cyclopentylmethanol	14486	1.82	5.50	6	0	0	0	0	1	0
dimethylbenzene	21071	1.25	8.00	2	6	0	0	0	0	0
dimethylcyclohexane	21071	1.25	8.00	8	0	0	0	0	0	0
dimethylcyclohexanediol	17120	1.54	6.50	8	0	0	0	0	0	2
dimethylcyclohexanol	19096	1.38	7.25	2	6	0	0	0	0	1
dimethylcyclohexanone	18437	1.43	7.00	2	5	0	1	0	0	0
dimethylphenol	19096	1.38	7.25	2	6	0	0	0	0	1
diphenyl ether	28973	0.91	11.00	0	12	0	0	1	0	0
ethoxybenzene	18437	1.43	7.00	2	6	0	0	1	0	0
ethoxycyclohexane	18437	1.43	7.00	8	0	0	0	1	0	0
guaiacol	13828	1.90	5.25	1	6	0	0	1	0	1
methoxycyclohexane	15803	1.67	6.00	7	0	0	0	1	0	0
methoxycyclohexanone	13169	2.00	5.00	6	0	0	1	1	0	0
methylanisole	15803	1.67	6.00	1	6	0	0	1	0	0
methylcyclohexane	18437	1.43	7.00	7	0	0	0	0	0	0
methylcyclohexanediol	14486	1.82	5.50	7	0	0	0	0	0	2
methylcyclohexanol	16462	1.60	6.25	7	0	0	0	0	0	1
methylcyclohexanone	15803	1.67	6.00	6	0	0	1	0	0	0
methylcyclohexene	18174	1.45	6.90	5	0	2	0	0	0	0
methylmethoxybenzene	18437	1.43	7.00	2	6	0	0	1	0	0
methylmethoxy-cyclohexane	18437	1.43	7.00	8	0	0	0	1	0	0
methylmethoxy-cyclohexanone	15803	1.67	6.00	7	0	0	1	1	0	0
phenol	13828	1.90	5.25	0	6	0	0	0	0	1
toluene	18437	1.43	7.00	1	6	0	0	0	0	0
trimethyl benzene	21729	1.21	8.25	3	6	0	0	0	0	1
veratrol	15803	1.67	6.00	2	6	0	0	2	0	0

Table S-1a. Analysis of product mixtures from the reaction of **phenol** over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate) ***Top:*** Reaction scheme showing calculated rate constants (k_{obs} in hr^{-1}) for conversion to specific products ($R^2 >$ 0.86). ***Bottom:*** Temporal evolution of the product mixture reported in percent of starting substrate and calculated from FID response of the GC-MS-FID and calibrated against decane as an internal standard (see above analysis section). Material balance: 82% at 3 h, 78% at 6 h, and 73% at 24 h.

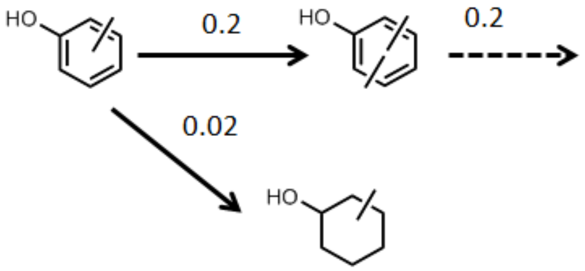


Compound	1h	2h	3h	6h	9h	12h	18h	24h
anisole	7.8	9.2	8.5	10.0	10.2	9.3	7.4	8.4
benzene	0.1	0.3	0.2	0.6	0.7	1.2	1.7	1.0
cresol	13.7	9.8	6.7	3.3	1.2	0.2	0.0	0.0
cyclohexane	0.0	0.2	0.3	0.6	0.7	1.0	1.1	1.0
cyclohexanol	18.4	29.4	28.3	13.7	9.0	6.3	2.8	5.2
cyclohexanone	0.9	1.1	1.1	0.4	0.3	0.3	0.0	0.1
dimethylbenzene	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1
dimethylcyclohexane	0.0	0.0	0.0	0.2	0.4	0.7	1.5	0.9
dimethylcyclohexanol	0.5	1.7	2.8	5.4	7.4	11.1	12.1	9.2
dimethylphenol	2.0	2.7	2.8	3.6	3.2	2.0	0.8	2.5
methoxycyclohexane	0.1	0.4	0.5	0.7	0.9	1.8	3.0	2.6
methylanisol	0.8	1.4	1.7	2.4	2.8	2.9	2.6	2.9
methylcyclohexane	0.0	0.1	0.3	0.4	0.8	1.8	3.8	2.4
methylcyclohexanol	9.0	19.4	24.5	34.0	36.4	39.0	32.2	32.8
methylcyclohexanone	0.6	0.8	1.1	1.2	1.2	1.2	0.9	1.0
methylmethoxycyclohexane	0.0	0.1	0.2	0.3	0.5	1.5	3.8	2.1
methylmethoxycyclohexanone	0.1	0.3	0.3	0.5	0.6	0.5	0.6	0.5
phenol	45.8	7.9	3.0	0.4	0.0	0.0	0.0	0.0
toluene	0.0	0.1	0.1	0.3	0.3	0.5	0.6	0.6

Table S-1b. Analysis of product mixtures from the reaction of **phenol** over the un-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg PMO, 20 µL decane, 1 mmol substrate). Product mixture reported in percent of starting substrate and calculated from FID response of the GC-FID and calibrated against decane as an internal standard (see above analysis section). Material balance: 86% at 18 h.

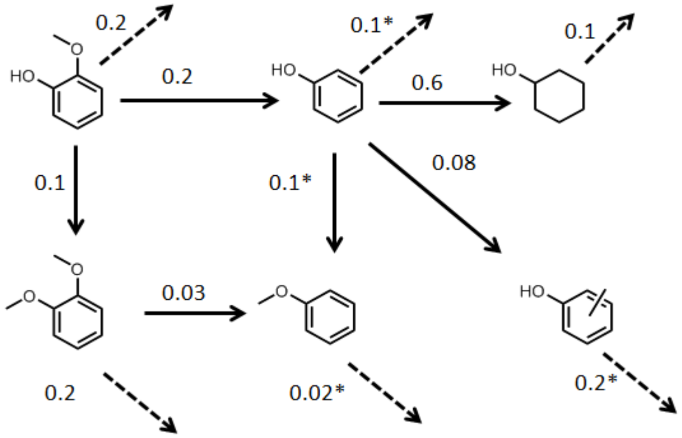
Compound	**0 h**	**18 h**
anisole	0.0	11.6
cresol	0.0	1.9
phenol	100.0	67.7

Table S-2. Analysis of product mixtures from the reaction of **cresol** (methyl phenol) over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate) ***Top:*** Reaction scheme showing calculated rate constants (k_{obs} in hr^{-1}) for conversion to specific products. ($R^2 > 0.89$) ***Bottom:*** Temporal evolution of the product mixture reported in percent of starting substrate and calculated from FID response of the GC-MS-FID and calibrated against decane as an internal standard (see above analysis section). Material balance 93% at 4 h.



Compound	**0**	**0.75**	**1**	**1.5**	**2**	**2.25**	**3**	**4**
cresol	100.0	80.7	67.8	67.9	57.1	51.6	46.4	48.9
dimethylcyclohexanol	0.0	0.0	0.0	0.0	0.3	0.0	0.5	0.3
dimethylphenol	0.0	14.6	19.3	21.3	24.4	35.3	37.5	33.0
methylcyclohexanol	0.0	0.8	1.6	1.5	4.9	1.8	4.3	5.6
methylcyclohexanone	0.0	0.1	0.2	0.1	0.3	0.1	0.3	0.3
methylmethoxybenzene	0.0	0.9	1.5	1.8	3.4	3.6	4.4	4.7
trimethylbenzene	0.0	0.0	0.0	0.0	0.4	0.0	0.4	0.3

Table S-3. Analysis of product mixtures from the reaction of **guaiacol** (2-methoxyphenol) over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate) ***Top:*** Reaction scheme showing calculated rate constants (k_{obs} in hr^{-1}) for conversion to specific products. ($R^2 > 0.89$) ***Bottom:*** Temporal evolution of the product mixture reported in percent of starting substrate and calculated from FID response of the GC-MS-FID and calibrated against decane as an internal standard (see above analysis section). Material balance >99% at 3 h, 83% at 6 h, 62% at 24 h.



Compound	1h	2h	3h	6h	9h	12h	18h	24h
anisole	0.0	0.5	2.2	4.4	5.8	6.7	7.7	4.7
benzene	0.0	0.0	0.0	0.2	0.4	0.7	2.0	0.5
cresol	1.2	1.5	3.7	1.7	0.1	0.0	0.0	0.0
cyclohexandiol	0.0	7.9	10.6	0.0	0.0	0.0	0.0	0.0
cyclohexane	0.0	0.1	1.0	3.4	3.0	3.7	4.2	3.3
cyclohexanol	0.0	3.0	14.9	18.8	10.2	8.3	3.0	7.1
cyclohexanone	0.0	0.1	0.7	1.6	1.1	1.1	1.1	0.7
cyclopentylmethanol	0.0	3.0	13.8	15.0	11.3	14.0	10.7	10.1
dimethylcyclohexane	0.0	0.0	0.1	0.5	0.5	0.7	1.8	0.5
dimethylcyclohexanol	0.1	1.4	4.1	3.2	3.7	4.5	4.7	4.0
dimethylphenol	0.5	1.8	2.0	1.0	0.3	0.3	0.0	0.2
guaiacol	87.1	42.8	8.1	0.0	0.0	0.0	0.0	0.0
methoxycyclohexane	0.0	0.1	0.7	2.1	2.6	3.4	5.0	2.0
methoxycyclohexanone	0.0	1.0	3.1	3.0	2.0	2.7	2.0	1.6
methylanisole	2.4	4.2	4.9	0.7	0.0	0.0	0.0	0.0
methylcyclohexane	0.0	0.1	0.3	1.3	1.8	2.3	4.5	1.9
methylcyclohexanol	0.0	0.6	5.0	14.1	18.3	20.6	20.5	21.6
methylcyclohexanone	0.0	0.0	0.3	1.0	0.5	0.7	0.7	0.7
phenol	2.1	8.7	10.5	0.2	0.0	0.0	0.0	0.0
toluene	0.0	0.0	0.1	0.2	0.2	0.4	0.4	0.2
veratrol	6.6	11.5	17.7	11.2	4.8	4.0	0.7	3.3

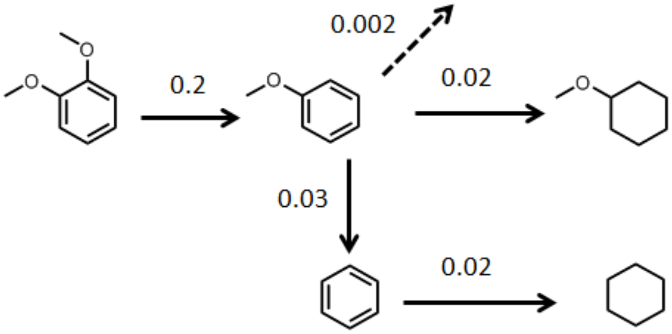
Table S-4. Analysis of product mixtures from the reaction of **anisole** over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate). Temporal evolution of the product mixture reported in percent of starting substrate and calculated from response area of the GC-MS and calibrated against decane as an internal standard (see above analysis section). The response factor for compounds marked with a star was approximated by compounds with the same atomic composition. Material balance >99% at 4 h, >99% at 6 h.

compound	**0h**	**1h**	**2h**	**3h**	**4h**	**6h**
anisole	100.0	98.8	94.2	94.9	95.0	82.4
benzene	0.0	0.5	3.0	6.8	5.7	17.1
cyclohexane	0.0	0.0	0.0	0.0	0.2	0.9
cyclohexanol	0.0	0.0	0.1	0.4	0.5	0.7
methoxycyclohexane*	0.0	0.0	0.2	0.6	0.3	2.0

Table S-5. Analysis of product mixtures from the reaction of **ethoxybenzene** over porous metal oxide catalyst. (310 °C, 3 mL MeOH, 0.100 g Cu20PMO, 20 µL decane, 1 mmol substrate). Temporal evolution of the product mixture reported in percent of starting substrate and calculated from FID response of the GC-MS-FID and calibrated against decane as an internal standard (see above analysis section). Material balance >99% at 6 h.

Compound	**3h**	**6h**
benzene	1.1	6.4
cyclohexanol	0.3	1.1
ethoxybenzene	98.4	88.0
ethoxycyclohexane	0.3	2.9
methylcyclohexanol	0.0	0.7

Table S-6. Analysis of product mixtures from the reaction of **veratrol** over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate) ***Top:*** Reaction scheme showing calculated rate constants (k_{obs} in hr^{-1}) for conversion to specific products. ($R^2 > 0.95$) ***Bottom:*** Temporal evolution of the product mixture reported in percent of starting substrate and calculated from FID response of the GC-MS-FID and calibrated against decane as an internal standard (see above analysis section). Material balance 98% at 3 h, 71% at 18 h.



Compound	1h	3h	12h	18h
anisole	10.7	39.7	45.2	27.3
benzene	0.1	2.1	12.5	18.1
cyclohexane	0.3	0.9	3.1	3.4
cyclohexanol	0.5	3.1	1.9	1.1
dimethylcyclohexanol	0.2	1.1	1.7	1.6
methoxycyclohexane	0.1	1.0	7.6	13.2
methylcyclohexane	0.0	0.3	1.2	2.2
methylcyclohexanol	0.4	2.6	4.7	3.8
toluene	0.0	0.1	0.4	0.7
veratrol	87.8	47.5	2.8	0.2

Table S-7. Analysis of product mixtures from the reaction of **benzyl phenyl ether** over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 50 mg Cu20PMO, 20 µL decane, 1 mmol substrate). Temporal evolution of the product mixture reported in percent of starting substrate and calculated from response area of the GC-MS and calibrated against decane as an internal standard (see above analysis section). Note, since benzyl phenyl ether conversion results in two products the total percent of starting substrate at complete conversion would be 200% with total conservation. Therefore, the material balance was calculated by dividing the summed moles of products by twice the initial moles of benzyl phenyl ether. The calculated material balances are thus 88% at 4 h, 97% at 6 h, 82% at 18 h. Note that toluene is >90% of that expected even at 18 h while phenol and phenolic products are lower.

compound	**0h**	**1h**	**2h**	**3h**	**4h**	**6h**	**8h**	**12h**	**18h**
benzylphenyl ether	100	15	1	0	0	0	0	0	0
phenol	0	76	60	24	3	0	0	0	0
toluene	0	81	91	96	92	88	88	93	90
phenol derived aromatics	0	8	19	20	18	15	20	13	16
phenol derived alkanes	0	6	26	39	63	72	60	64	59
unassigned products	0	0	1	10	12	13	15	15	18

Table S-7b. Analysis of product mixtures from the reaction of **benzyl phenyl ether** over the un-doped Mg/Al (3/1) PMO catalyst . (310 °C, 3 mL MeOH, 50 mg PMO, 20 µL decane, ca. 1 mmol substrate). Product mixture reported in percent of starting substrate and calculated from FID response of the GC-FID and calibrated against decane as an internal standard (see above analysis section). The “dimeric” products were products whose M.W. as indicated by GC-MS suggested two rings. The response factor for these were based on an ECN of 12.5. Material balance: 76% at 3 h, 58% at 18 h with the caveat noted above in S-7a.

compound	**0h**	**1h**	**3h**	**6h**	**18h**	**24h**
anisole	0.0	0.0	0.3	0.7	8.1	5.1
benzyl alcohol	0.0	0.5	1.1	1.8	4.6	2.9
benzyl phenyl ether	100.0	75.3	48.3	41.0	1.3	0.4
cresol	0.0	0.1	0.7	1.8	10.1	8.4
methylanisole	0.0	0.3	0.5	0.8	2.6	1.0
phenol	0.0	3.0	13.7	21.8	6.3	13.2
toluene	0.0	2.8	17.6	24.7	44.5	47.9
xylenol	0.0	0.0	0.1	0.3	4.6	2.8
dimeric products	0.0	1.9	11.6	16.6	16.7	20.1

Table S-8. Analysis of product mixture from the reaction of **2-phenoxy-1-phenylethan-1-one** over porous metal oxide catalyst (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate). Product mixture reported in mol percent of products detected and calculated from FID response of the GC-MS-FID and calibrated against decane as an internal standard.

Compound	**6h**
benzene	0.5
cresol	3.5
cyclohexane	0.5
cyclohexanol	14.1
dimethylcyclohexanol	1.4
dimethylphenol	3.5
ethylbenzene	34.7
methoxycyclohexane	0.5
methylanisole	1.5
methylcyclohexane	0.4
methylcyclohexanol	19.9
methylcyclohexanone	0.7
propylbenzene	16.8
toluene	1.9

Table S-9. Analysis of product mixtures from the reaction of **cyclohexanol** over the copper-doped porous metal oxide catalyst. (310 °C, 3 mL MeOH, 100 mg Cu20PMO, 20 µL decane, 1 mmol substrate). Temporal evolution of the product mixture reported in percent of starting substrate and calculated from response area of the GC-MS and calibrated against decane as an internal standard (see above analysis section). The response factor for compounds marked with a star was approximated by compounds with the same atomic composition. Material balance >99% at 3 h, >99% at 6 h.

compound	**0**	**1**	**2**	**3**	**4.15**	**6**
cyclohexane	0.0	0.2	0.7	0.9	1.6	2.1
cyclohexanol	100.0	88.0	66.3	73.9	47.9	39.8
methylcyclohexanol	0.0	13.8	28.3	30.9	48.0	58.3
other compounds*	0.0	0.6	1.8	2.2	4.0	5.2

Figure S-1. Comprehensive reaction network of mono-aromatics over the copper-doped porous metal oxide catalyst.