

SUPPORTING INFORMATION

Design of a High-Pressure Flow-Reactor System for Catalytic Hydrodeoxygenation: Guaiacol Conversion Catalyzed by Platinum Supported on MgO

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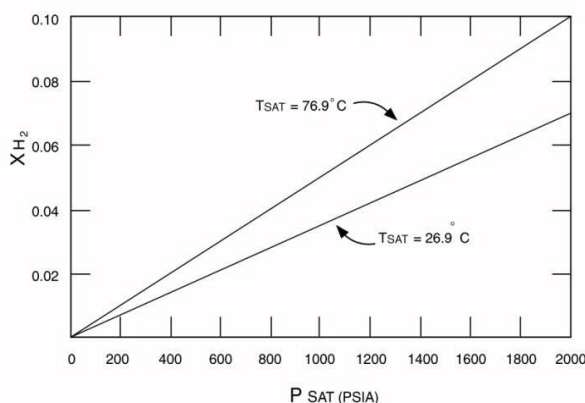


Figure S1 Calculated mole fractions of H₂ dissolved in *n*-hexadecane at 26.9 °C and at 76.9 °C. The calculations are based on the N.G.P.A. version of the Chao-Seader vapor-liquid equilibrium equations; the estimated accuracy is $\pm 10\%$. Details are given in M. V. Bhide, PhD Dissertation, University of Delaware, 1979.

Notes regarding plug flow approximation in the reactor. According to the guidelines in H. Kramers and K. R. Westerterp, *Elements of Chemical Reactor Design and Operation*, Academic Press, New York, 1963, p 95, the flow was well approximated as plug flow, with the ratio of the length of the packed section of the reactor to the average particle diameter being > 100 and the ratio of the particle diameter to the tube diameter was < 0.1 . Because our conversions were much less than one, the approximation is excellent, with any errors related to deviations from plug flow estimated to be less than the analytical errors affecting the determinations of conversions.

Table S1 List of experiments: measurement of guaiacol conversions with high-pressure reactor system.

Temperature, C	Pressure, psi	Catalyst	Catalyst Amount, g
250	600	Pt/MgO	0.1
250	800	Pt/MgO	0.1
250	1000	Pt/MgO	0.1
250	1000	Pt/MgO	recycle 1
250	1000	Pt/MgO	recycle 1
250	1000	Pt/MgO	0.05
250	1000	Pt/MgO	0.02
250	1000	Pt/MgO	0.01
200	1000	Pt/MgO	0.1
150	1000	Pt/MgO	0.1
250	1000	CoMo/Al ₂ O ₃	0.1
200	1000	CoMo/Al ₂ O ₃	0.1
150	1000	CoMo/Al ₂ O ₃	0.1

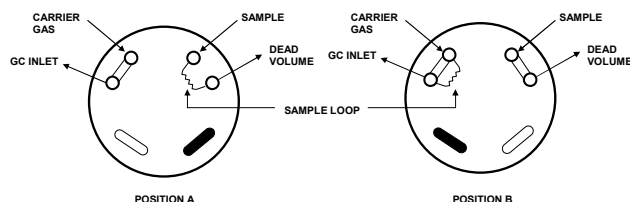
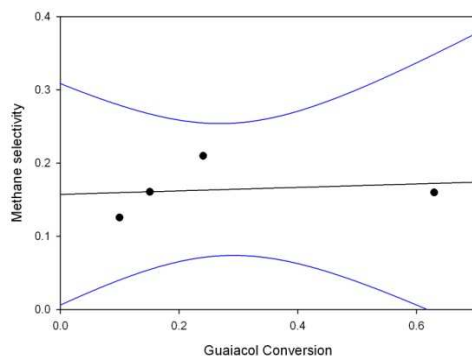


Figure S.2 Schematic representation of operation of high-pressure sample valve.



(1) **Figure S3** Selectivity for the formation of methane in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H₂ at 250°C and 1000 psi; error bars were determined in replicate experiments at conversions of approximately 0.10, 0.15, 0.24, and 0.63. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits, which are shown by the curved lines) indicate primary products. Methane is a primary product in this case. Details of the method are available in the following: Bhole, N. A.; Klein, M. T.; Bischoff, K. B. The Delplot Technique: a New Method for Reaction Pathway Analysis. *Ind. Eng. Chem. Res.* **1990**, *29*, 313-316.

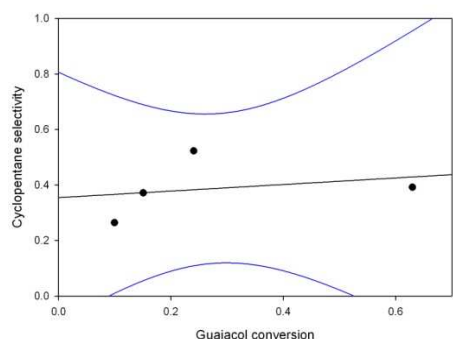


Figure S4 Selectivity for the formation of cyclopentane in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H₂ at 250°C and 1000 psi; error bars were determined in replicate experiments at conversions of approximately 0.10, 0.15, 0.24 and 0.63. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products. Cyclopentane is a non-primary product in this case.

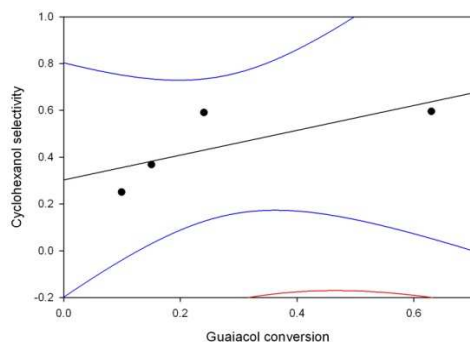
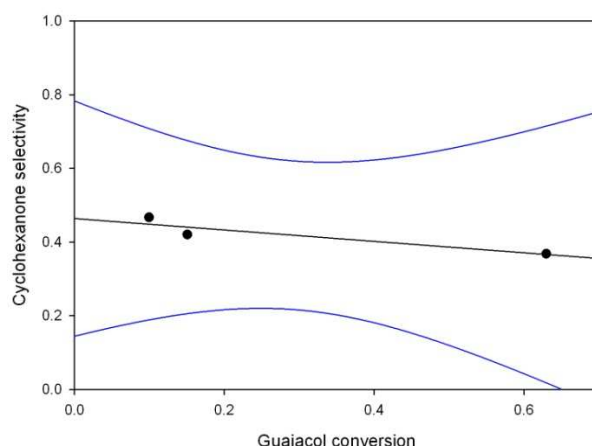


Figure S5 Selectivity for the formation of cyclohexanol in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H₂ at 250°C and 1000 psi; error bars were determined in replicate experiments at conversions of approximately 0.10, 0.15, 0.24 and 0.63. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products. Cyclohexanol is a non-primary product in this case.



FigureS6 Selectivity for the formation of cyclohexanone in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H_2 at $250^\circ C$ and 1000 psi; error bars were determined in replicate experiments at conversions of approximately 0.10, 0.15, 0.24 and 0.63. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products. Cyclohexanone is indicated to be a primary product in this case. **Note however:** Although the plot points to cyclohexanone as a primary product formed directly from guaiacol, the chemistry of this reaction seems implausible, and we regard it as more likely that cyclohexanone is a non-primary product formed after either saturation of the aromatic ring or an oxygen removal (or both).

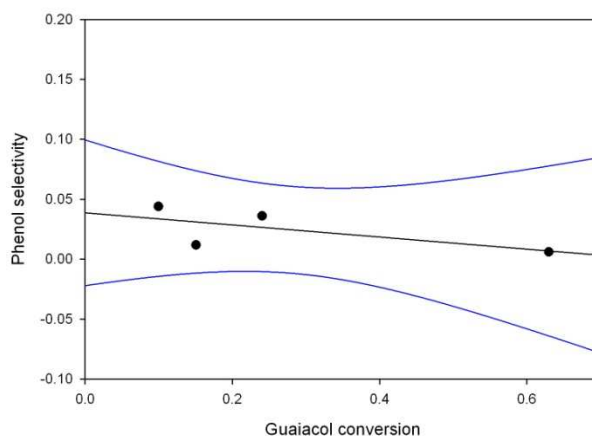


Figure S7 Selectivity for the formation of phenol in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H_2 at $250^\circ C$ and 1000 psi; error bars were determined in replicate experiments at conversions of approximately 0.10, 0.15, 0.24 and 0.63. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products. Phenol is indicated as a non-primary product in this case. **Note however:** Although the plot indicates that phenol is a non-primary product formed directly from guaiacol, this result contradicts the previous analysis of data obtained in a low-pressure system (as cited in the main text), whereby phenol is always a primary product. It might be possible that the aromatic ring of guaiacol is first hydrogenated before any oxygen removal occurs in the high-pressure environment. Thus, phenol would then be non-primary product.

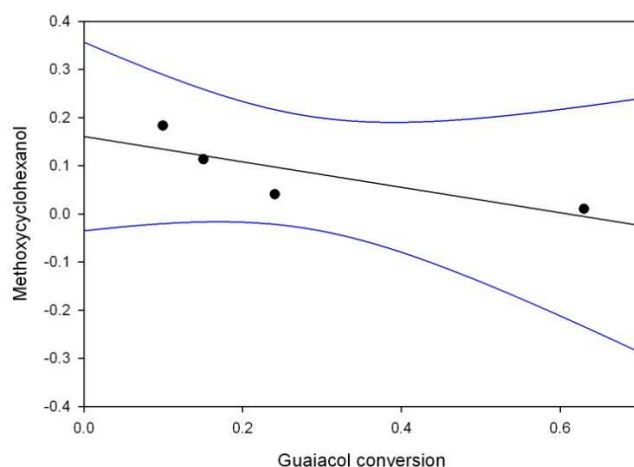


Figure S8 Selectivity for the formation of methoxycyclohexanol in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H₂ at 250°C and 1000 psi; error bars were determined in replicate experiments at conversions of approximately 0.10, 0.15, 0.24 and 0.63. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products. Methoxycyclohexanol is indicated to be a non-primary product in this case. **Note however:** Although the plot indicates that methoxycyclohexanol is a non-primary product formed directly from guaiacol, we regard it as more likely that the aromatic ring of guaiacol is hydrogenated and is converted to methoxycyclohexanol as a primary product. This appears to be the more plausible pathway in this case.