

ELECTRONIC SUPPLEMENTARY INFORMATION

Insights into the catalytic activity and surface modification of MoO₃ during the hydrodeoxygenation of lignin-derived model compounds into aromatic hydrocarbons under low hydrogen pressures

Teerawit Prasomsri, Manish Shetty, Karthick Murugappan and Yuriy Román-Leshkov*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA, 02139

E-mail: yroman@mit.edu

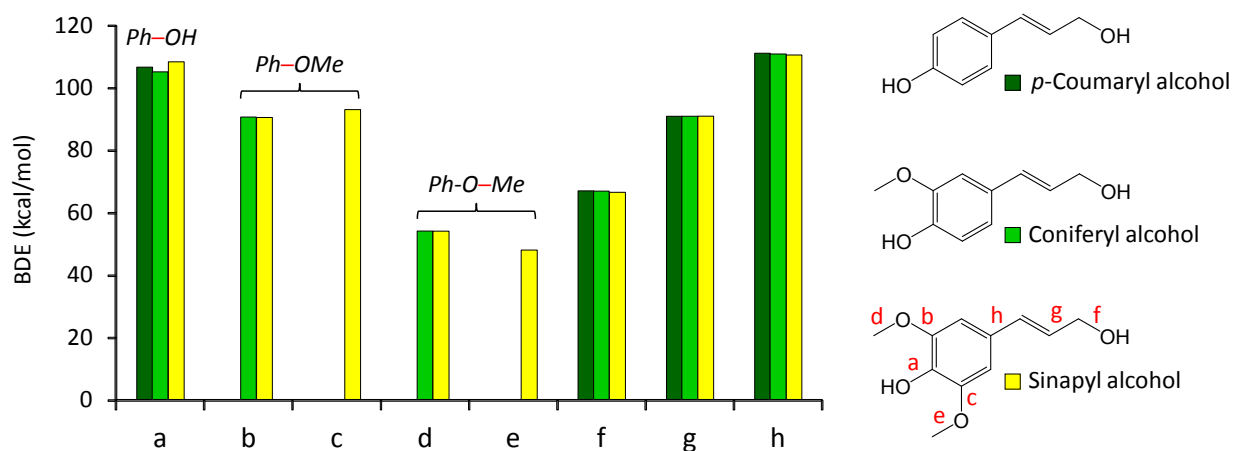


Fig. S1 Comparison of the homolytic bond dissociation energies (BDEs) of monolignols calculated by using the B3LYP/6-311+G(d,p) level of theory at 593 K in gas phase.

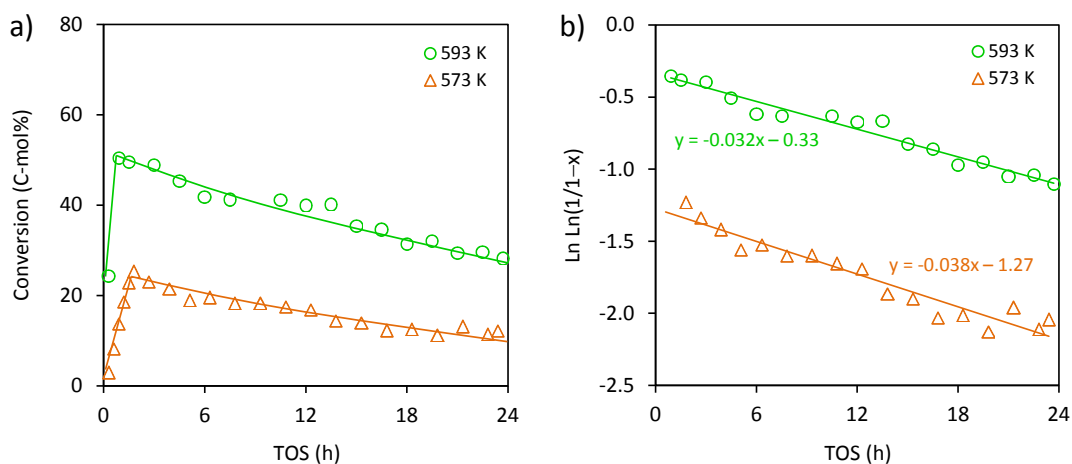


Fig. S2 a) Long-run experiments on conversion of *m*-cresol over a period of 24 h, and b) the corresponding catalyst deactivation profiles. Reaction conditions: $P_{\text{Total}} = 1.013$ bar (0.015 bar P_{Feed} , balance H_2), $W/F = 0.035$ $\text{g}_{\text{Cat}} (\text{mmol}_{\text{Feed}} \text{h}^{-1})^{-1}$, and no H_2 pre-reduction.

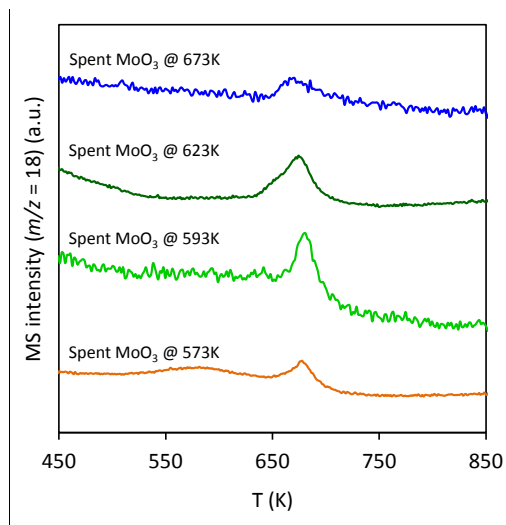


Fig. S3 TGA-MS traces for the evolution of H_2O ($m/z = 18$) from the spent MoO_3 catalysts. The spent MoO_3 samples derived from the experiments shown in Fig. 2 were passivated using 1 vol% O_2/N_2 mixture at room temperature for 1 h prior to the analysis.

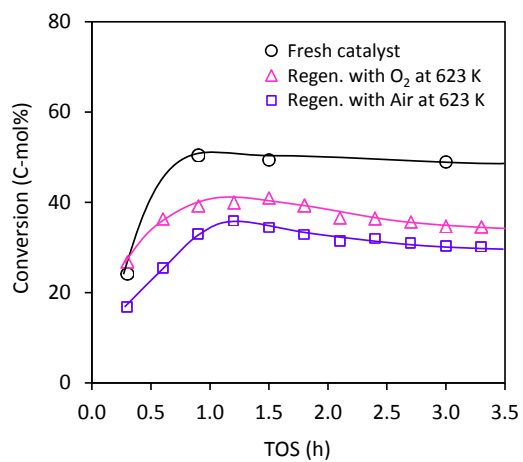


Fig. S4 Unsuccessful regeneration of the MoO₃ catalyst using conversion of *m*-cresol as a probe reaction. Reaction conditions: $P_{\text{Total}} = 1.013$ bar (0.015 bar P_{Feed} , balance H₂), $W/F = 0.035$ g_{Cat} (mmol_{Feed} h⁻¹)⁻¹, and no pre-reduction. Regeneration conditions: $T = 623$ K, $P_{\text{Total}} = 1.013$ bar (100% O₂ or air) for 3 h.

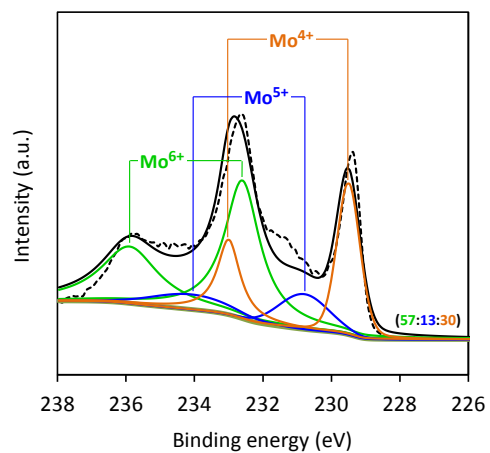
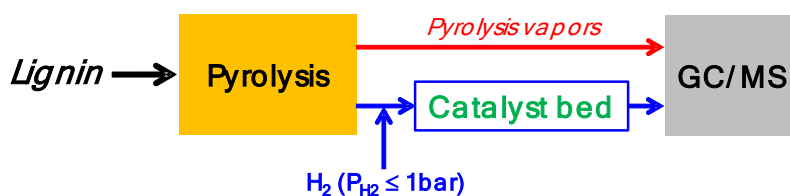


Fig. S5 XPS of the Mo (3d) energy region of the passivated MoO₂ samples. The numbers in parentheses are the corresponding oxidation state percentages of Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺, respectively.

As a proof of concept, a real lignin-derived feed was subjected to HDO conditions using a modified micro-pyrolyser (Pyroprobe 5150, CDS Analytical) to simulate an *ex situ* catalytic pyrolysis scenario (see scheme S1). A pulse of lignin-derived compounds generated from the pyrolysis of kraft lignin (Sigma-Aldrich) was sent directly to a GC/MS for analysis or mixed with an H₂ stream and sent through a MoO₃ catalyst bed prior to analysis. As shown in Fig. S6, alkylphenolics obtained by fast pyrolysis of kraft lignin were readily converted into a mixture of alkylaromatic hydrocarbons using the MoO₃ catalyst. Although this setup does not allow calculating a mass balance, these qualitative results show that MoO₃ is a promising HDO catalyst capable of upgrading real lignin feeds. Further investigations using lignocellulosic feeds and reducible metal oxides are currently underway.



Scheme S1. Catalytic upgrading of lignin-pyrolysis vapours using Py-GC/MS technique.

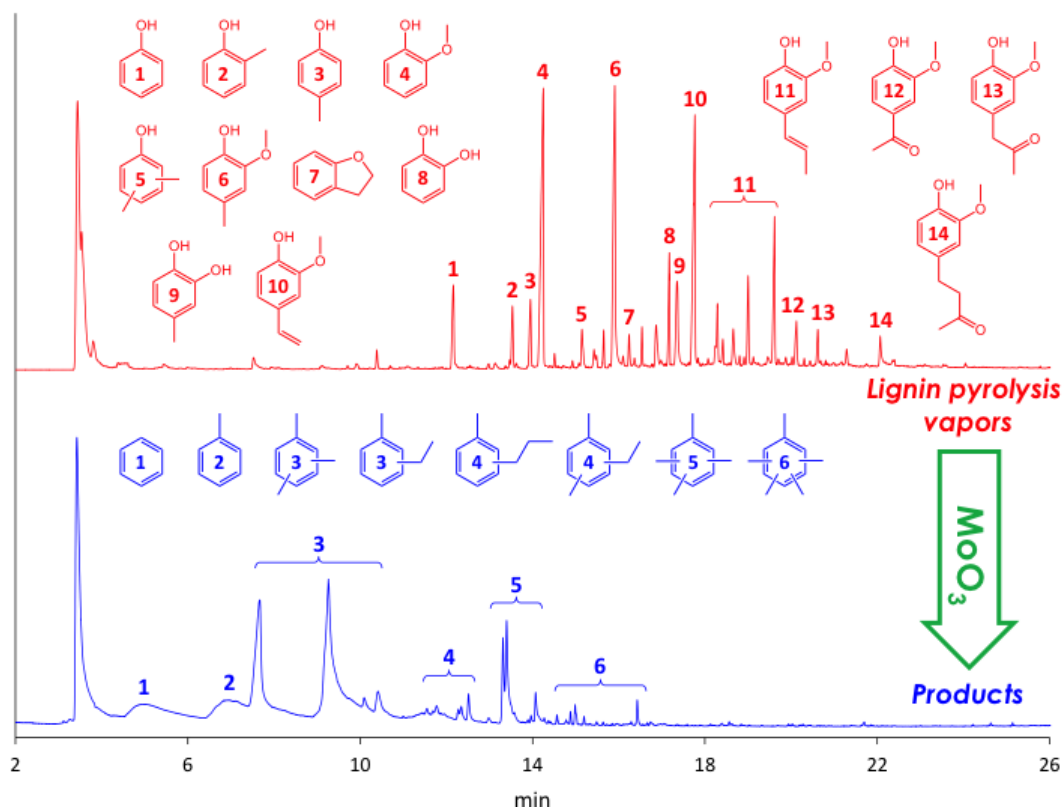


Fig. S6. The GC chromatograms demonstrating the analysis of lignin-pyrolysis vapours before and after the catalytic upgrading using MoO₃ catalyst. Pyrolysis lignin was conducted in a Pyroprobe using the following procedures: pyrolysis temperature = 923 K, ramp rate = 10 K/s, pyrolysis duration = 30 s, and sample loading ~ 1 mg. Reaction conditions: T = 623 K, P_{H₂} < 1 bar, MoO₃ loading = 20 mg. GC analysis method: start at 313 K, hold for

5 min, increased at 10 K/min to 533 K, and hold for 25 min, split ratio of 50:1, carrier gas 1 mL/min. Peak identification was achieved by means of the NIST08 mass spectrum library.