Thermal annealing effects on hydrothermally synthesized unsupported MoS$_2$ for enhanced deoxygenation of Propylguaiacol and Kraft lignin

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| Element          | Impurity (mg/kg) | Manganese (mg/kg) |
|------------------|------------------|-------------------|
| Aluminium, Al     | 18               | Mn                 |
| Antimony, Sb      | 0.06             | Mo                 |
| Arsenic, As       | 0.08             | Na                 |
| Barium, Ba        | 0.04             | Nd                 |
| Beryllium, Be     | 0.013            | Nb                 |
| Lead, Pb          | 0.04             | Ni                 |
| Boron, B          | 22               | Os                 |
| Bromine, Br       | 1.2              | Au                 |
| Cerium, Ce        | 0.012            | Pt                 |
| Gadolinium, Gd    | 0.016            | Pr                 |
| Dysprosium, Dy    | <0.005           | Re                 |
| Erbium, Er        | <0.005           | Rh                 |
| Europium, Eu      | <0.005           | Ru                 |
| Phosphorus, P     | 12               | Sm                 |
| Gadolinium, Gd    | <0.005           | Eu                 |
| Gallium, Ga       | 0.03             | Se                 |
| Germanium, Ge     | 0.03             | Ag                 |
| Gold, Au          | <0.005           | Sc                 |
| Hafnium, Hf       | <0.005           | Sr                 |
| Holmium, Ho       | <0.005           | S                  |
| Iridium, Ir       | <0.005           | Ta                 |
| Iodine, I         | 0.5              | Te                 |
| Iron, Fe          | 0.17             | Sn                 |
| Cadmium, Cd       | 200              | Tb                 |
| Calcium, Ca       | 1100             | Ti                 |
| Silicon, Si       | 6000             | Th                 |
| Cobalt, Co        | 0.08             | Th                 |
| Copper, Cu        | 0.9              | U                  |
| Chromium, Cr      | 0.3              | V                  |
| Mercury, Hg       | <0.005           | Bi                 |
| Lanthanum, La     | 0.007            | W                  |
| Lithium, Li       | 0.07             | Y                  |
| Lutetium, Lu      | <0.005           | Zr                 |
| Magnesium, Mg     | 21               | Zn                 |

Figure S1 ICP analysis of impurities in kraft lignin.
Table S1 Elemental analysis for kraft lignin.

| Elemental analysis (%) | Wt% |
|------------------------|-----|
| C                      | 62.1|
| H                      | 5.85|
| N                      | 0.35|
| S                      | 2.18|
| O                      | 29.5*|

*by difference and neglecting other impurities

Figure S2 Nitrogen adsorption-desorption isotherms for studied catalysts.
Figure S3 Additional HRTEM images of a-c) MoS$_2$-12, d-f) MoS$_2$-12a, g-i) MoS$_2$-24, and j-l) MoS$_2$-24a.
Figure S4a) Distribution of the number of stacks and b) MoS\(_2\) slab length for different unsupported MoS\(_2\).

Figure S5 Comparison of PG conversion and product selectivity for HDO of PG over MoS\(_2\)-24 following an annealing treatment under different atmosphere (air or N\(_2\)) at 400 °C for 2 h. Reaction conditions: 50 bar total H\(_2\) pressure, 300 °C, and 1000 rpm.
Figure S6 Reaction product distribution for HDO of PG over a) Bulk MoS\textsubscript{2} b) 13.2 wt\% MoS\textsubscript{2} supported on alumina at 50 bar total H\textsubscript{2} pressure, 300 °C and 1000 rpm.

Figure S7 GC spectrum of the lignin fraction obtained from the hydrotreatment of kraft lignin over commercial MoS\textsubscript{2} (blue line) and MoS\textsubscript{2}-12a (black line). Reaction conditions: 3:1 lignin to catalyst ratio, 340 °C, 40 bar initial H\textsubscript{2} pressure, and 1000 rpm. The major compounds were labeled in the spectrum as (1) Methylcyclopentane, (2) Cyclohexane, (3) Methylcyclohexane, (4) Ethylcyclopentane, (5) Toluene, (6) Ethylcyclohexane, (7) 1,3-dimethylbenzene, (8) Propylcyclohexane, (9) Propylbenzene, (10) Guaiacol, (11) Creosol, (12) 4-ethyl-2-methoxyphenol and (13) Propylguaiacol.

Table S2 Products identified from GC-MS spectra and product yields for hydrotreatment of Kraft lignin over bulk MoS\textsubscript{2} and MoS\textsubscript{2}-12a. Reaction conditions: 3:1 lignin to catalyst mass ratio, 340 °C, 40 bar initial H\textsubscript{2} pressure, and 1000 rpm.

| Retention time (min) | Compound identified          | Compound chemical formula | FID peak area (Bulk MoS\textsubscript{2}) | Bulk MoS\textsubscript{2} Product yield (area %) | FID peak area (MoS\textsubscript{2}-12a) | MoS\textsubscript{2}-12a Product yield (area %) |
|---------------------|-------------------------------|---------------------------|------------------------------------------|---------------------------------------------|-----------------------------------------|---------------------------------------------|
| 7.135               | Methylcyclopentane            | C\textsubscript{6}H\textsubscript{12} | -                                        | -                                          | 2.10 \times 10\textsuperscript{6}     | 2.53                                        |
| 8.089               | Cyclohexane                    | C\textsubscript{6}H\textsubscript{10} | 6.19 \times 10\textsuperscript{5}        | 1.9                                        | 1.56 \times 10\textsuperscript{7}     | 18.83                                       |
|     | Common Name                      | Molecular Formula | N | K      |   |     |
|-----|---------------------------------|-------------------|---|--------|---|-----|
| 16.034 | n-butylbenzene              | C_{10}H_{14}      | - | -      |   | 5.67 × 10^5 | 0.68 |
| 16.136 | Cyclopropylbenzene        | C_{6}H_{10}       | - | -      |   | 1.08 × 10^5 | 1.31 |
| 16.321 | 1-methyl-3-propylbenzene   | C_{10}H_{14}      | - | -      |   | 9.61 × 10^5 | 1.16 |
| 16.441 | n-butylbenzene              | C_{10}H_{14}      | - | -      |   | 3.89 × 10^5 | 0.47 |
| 16.588 | 3-methylphenol             | C_{7}H_{5}O       | 2.04 × 10^6 | 6.25 | - | -   |
| 16.944 | Guaiacol                   | C_{8}H_{10}O_{2}  | 5.13 × 10^6 | 15.71 | - | -   |
| 17.134 | (2-Methylbutyl)cyclohexane | C_{11}H_{22}      | - | -      |   | 3.31 × 10^5 | 0.40 |
| 17.832 | Pentylcyclohexane           | C_{11}H_{22}      | - | -      |   | 5.45 × 10^4 | 0.66 |
| 17.888 | 2,4-dimethylphenol          | C_{8}H_{10}O      | 2.89 × 10^5 | 0.88 | - | -   |
| 17.919 | (3-methyl-2-butenyl)-benzene| C_{11}H_{14}      | - | -      |   | 3.36 × 10^4 | 0.41 |
| 18.151 | 3-ethylphenol | C₈H₁₀O | 1.43 \times 10^6 | 4.37 | - | - |
| 18.152 | 2,5-Dimethylphenyl methyl carbinol | C₁₀H₁₄O | - | - | 1.03 \times 10^6 | 1.24 |
| 18.395 | 1,2,3,4-tetrahydro-Naphthalene | C₁₀H₁₂ | - | - | 8.78 \times 10^5 | 1.06 |
| 18.658 | Creosol | C₉H₁₀O₂ | 7.09 \times 10^6 | 21.71 | - | - |
| 19.247 | 3,4-dimethoxyltoluene | C₉H₁₂O₂ | 4.63 \times 10^5 | 1.42 | - | - |
| 19.249 | 1,2,3,4-tetrahydro-2-methyl-Naphthalene | C₁₁H₁₄ | - | - | 5.24 \times 10^5 | 0.63 |
| 19.563 | 3-propylphenol | C₉H₁₂O | 1.21 \times 10^6 | 3.69 | - | - |
| 19.927 | 4-ethyl-2-methoxyphenol | C₉H₁₂O₂ | 4.73 \times 10^6 | 14.50 | - | - |
| 20.460 | 4-ethyl-1,2-dimethoxybenzene | C₁₀H₁₄O₂ | 3.93 \times 10^5 | 1.20 | - | - |
| 20.634 | 2,5-diol-p-cymene | C₁₀H₁₄O₂ | 2.71 \times 10^5 | 0.83 | - | - |
| 20.884 | 4-(2-propenyl)-phenol | C₉H₁₀O | 6.56 \times 10^5 | 2.01 | - | - |
| 21.171 | 2-methoxy-4-propylphenol | C₁₀H₁₄O₂ | 2.76 \times 10^6 | 8.28 | - | - |
| 21.502 | 4-(1-methylethyl)-benzaldehyde | C₁₀H₁₂O | 1.27 \times 10^6 | 3.89 | - | - |