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# Enhancing the performance of heterogeneous palladium based catalysts in the mild reductive depolymerization of Soda lignin through addition of a non-noble metal and tuning of the preparation strategy.

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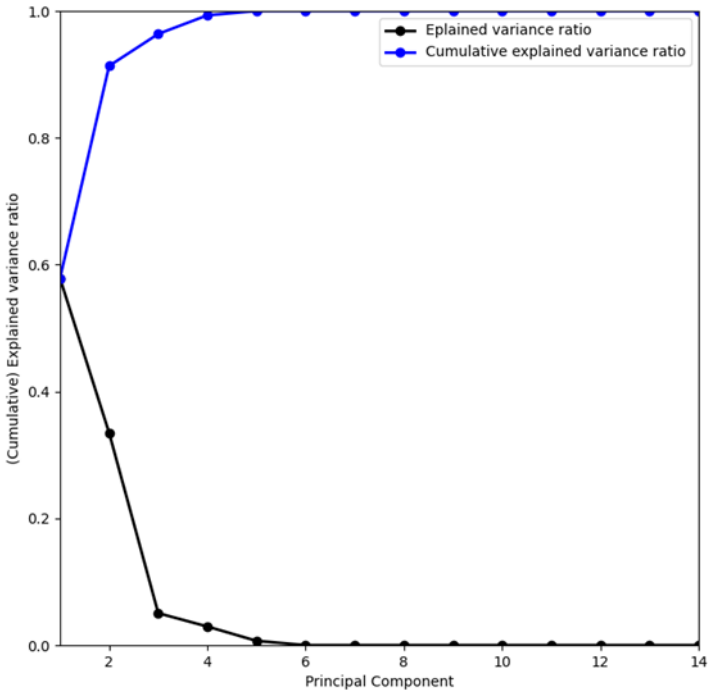


**Figure S1:** Scree plot representing the explained variance ratio (black) and the cumulated explained variance ratio (blue) as a function of the number of principal components.

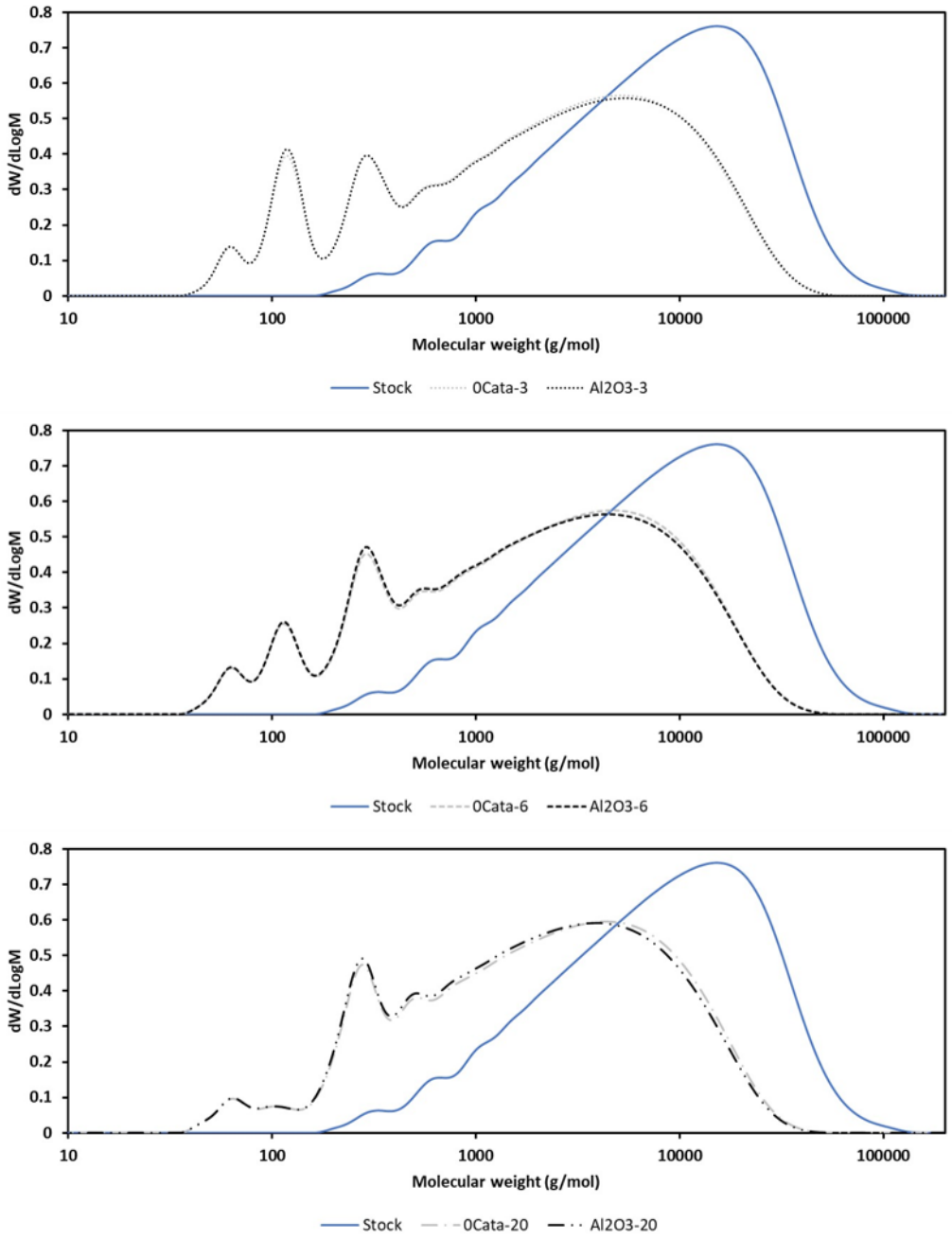


**Figure S2:** Molecular weight distributions for 0Cata (grey) and Al2O3 (black) compared to the lignin stock solution (blue) after 3 h (top), 6 h (middle) and 20 h (bottom) of reaction time.

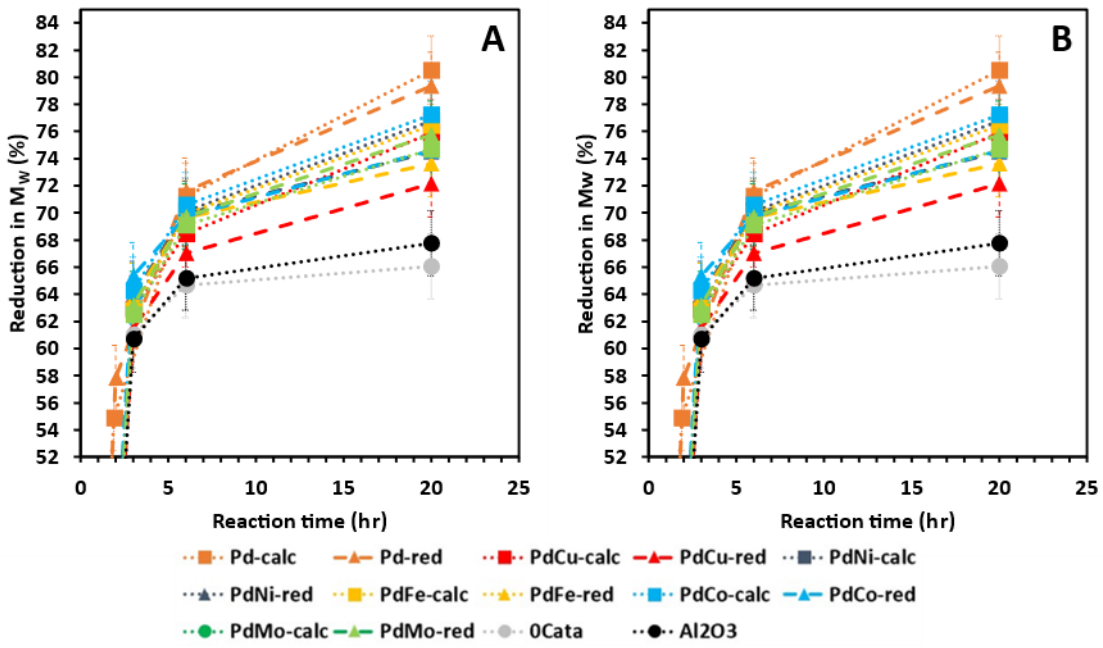


**Figure S3:** Reduction in Mw (A) and increase in PDI (B) as a function of reaction time for 0Cata, Al2O3 and all Pd(X)-calc/red variations.

**Table S1:** reaction time, batch time, reduction in Mw (with numerical Mw values), Mw reduction rate, increase in PDI (with numerical PDI values) and PDI increase rate for all performed experiments.

| Sample | Reaction time (h) | Batch time (mmol Pd*s) | Reduction in $M_W$ (%) ($M_W$ (g/mol)) | $M_W$ reduction rate (%/(mmol Pd*s) | Increase in PDI (%) (PDI) | PDI increase rate (%/(mmol Pd*s) |
|---|---|---|---|---|---|---|
| Stock solution | 0 | 0 | 0 (12938) | Not applicable | 0% (4) | Not applicable |
| 0Cata | 3 | Not applicable | 61.03 +- 2.45 (5042) | Not applicable | 131.75 +- 11.27 (9.27) | Not applicable |
| | 6 | Not applicable | 64.66 +- 2.38 (4572) | Not applicable | 96.75 +- 11.84 (7.87) | Not applicable |
| | 20 | Not applicable | 66.05 +- 2.39 (4392) | Not applicable | 66 +- 9.08 (6.64) | Not applicable |
| Al2O3 | 3 | Not applicable | 60.68 +- 2.45 (5087) | Not applicable | 137.25 +- 11.66 (9.49) | Not applicable |
| | 6 | Not applicable | 65.19 +- 2.38 (4504) | Not applicable | 97.25 +- 11.89 (7.89) | Not applicable |
| | 20 | Not applicable | 67.75 +- 2.4 (4172) | Not applicable | 64 +- 8.88 (6.56) | Not applicable |
| Pd-calc | 2 | 100.98 | 54.89 +- 2.41 (5836) | 0.544 +- 0.024 | 168.25 +- 13.86 (10.73) | 1.666 +- 0.137 |
| | 6 | 322.72 | 71.22 +- 2.44 (3724) | 0.221 +- 0.008 | 160 +- 16.65 (10.4) | 0.496 +- 0.052 |
| | 20 | 1075.74 | 80.52 +- 2.53 (2520) | 0.075 +- 0.002 | 110 +- 12.92 (8.4) | 0.102 +- 0.012 |
| Pd-red | 2 | 104.53 | 57.82 +- 2.43 (5457) | 0.553 +- 0.023 | 168.5 +- 13.88 (10.74) | 1.612 +- 0.133 |
| | 6 | 313.59 | 71.6 +- 2.44 (3674 ) | 0.228 +- 0.008 | 155.75 +- 16.35 (10.23) | 0.497 +- 0.052 |
| | 20 | 1045.29 | 79.33 +- 2.51 (2674) | 0.076 +- 0.002 | 117.75 +- 13.53 (8.71) | 0.113 +- 0.013 |
| PdCu-calc | 3 | 99.45 | 62.91 +- 2.47 (4799) | 0.633 +- 0.025 | 167.25 +- 13.79 (10.69) | 1.682 +- 0.139 |
| | 6 | 198.91 | 68.44 +- 2.41 (4083) | 0.344 +- 0.012 | 161 +- 16.72 (10.44) | 0.809 +- 0.084 |
| | 20 | 663.03 | 75.88 +- 2.48 (3121) | 0.114 +- 0.004 | 126.75 +- 14.22 (9.07) | 0.191 +- 0.021 |
| PdCu-red | 3 | 110.11 | 61.48 +- 2.46 (4984) | 0.558 +- 0.022 | 140.5 +- 11.89 (9.62) | 1.276 +- 0.108 |
| | 6 | 220.22 | 67.04 +- 2.4 (4265) | 0.304 +- 0.011 | 106.75 +- 12.66 (8.27) | 0.485 +- 0.057 |
| | 20 | 734.07 | 72.13 +- 2.44 (3606) | 0.098 +- 0.003 | 80.25 +- 10.42 (7.21) | 0.109 +- 0.014 |
| PdNi-calc | 3 | 120.77 | 62.87 +- 2.47 (4804) | 0.521 +- 0.02 | 165 +- 13.63 (10.6) | 1.366 +- 0.113 |
| | 6 | 241.53 | 70.12 +- 2.43 (3866) | 0.29 +- 0.01 | 149 +- 15.86 (9.96) | 0.617 +- 0.066 |
| | 20 | 805.11 | 76.76 +- 2.49 (3007) | 0.095 +- 0.003 | 115.5 +- 13.35 (8.62) | 0.143 +- 0.017 |
| PdNi-red | 3 | 94.38 | 63.94 +- 2.48 (4665) | 0.678 +- 0.026 | 145 +- 12.21 (9.8) | 1.536 +- 0.129 |
| | 6 | 188.76 | 69.93 +- 2.42 (3891) | 0.37 +- 0.013 | 132.25 +- 14.63 (9.29) | 0.701 +- 0.078 |
| | 20 | 629.21 | 74.52 +- 2.47 (3296) | 0.118 +- 0.004 | 89.5 +- 11.23 (7.58) | 0.142 +- 0.018 |
| PdFe-calc | 3 | 188.76 | 62.84 +- 2.47 (4808) | 0.673 +- 0.026 | 167.75 +- 13.83 (10.71) | 1.797 +- 0.148 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 6 | 93.37 | 69.95 +- 2.42 (3888) | 0.375 +- 0.013 | 142.5 +- 15.39 (9.7) | 0.763 +- 0.082 |
| | 20 | 622.44 | 76.43 +- 2.48 (3049) | 0.123 +- 0.004 | 102.75 +- 12.34 (8.11) | 0.165 +- 0.02 |
| | 3 | 106.56 | 63.8 +- 2.48 (4683) | 0.599 +- 0.023 | 165.5 +- 13.67 (10.62) | 1.553 +- 0.128 |
| PdFe-red | 6 | 213.12 | 69.67 +- 2.42 (3924) | 0.327 +- 0.011 | 144.75 +- 15.55 (9.79) | 0.679 +- 0.073 |
| | 20 | 710.39 | 73.64 +- 2.46 (3411) | 0.104 +- 0.003 | 101.5 +- 12.24 (8.06) | 0.143 +- 0.017 |
| | 3 | 94.38 | 64.26 +- 2.48 (4624) | 0.681 +- 0.026 | 167 +- 13.78 (10.68) | 1.769 +- 0.146 |
| PdCo-calc | 6 | 188.76 | 70.57 +- 2.43 (3808) | 0.374 +- 0.013 | 144 +- 15.5 (9.76) | 0.763 +- 0.082 |
| | 20 | 629.21 | 77.25 +- 2.49 (2944) | 0.123 +- 0.004 | 111.5 +- 13.04 (8.46) | 0.177 +- 0.021 |
| | 3 | 83.22 | 65.34 +- 2.49 (4484) | 0.785 +- 0.03 | 139.5 +- 11.82 (9.58) | 1.676 +- 0.142 |
| PdCo-red | 6 | 166.43 | 69.74 +- 2.42 (3915) | 0.419 +- 0.015 | 112.25 +- 13.1 (8.49) | 0.674 +- 0.079 |
| | 20 | 554.78 | 74.6 +- 2.47 (3286) | 0.134 +- 0.004 | 86.25 +- 10.95 (7.45) | 0.155 +- 0.02 |
| | 3 | 96.92 | 62.5 +- 2.47 (4852) | 0.645 +- 0.025 | 167.75 +- 13.83 (10.71) | 1.731 +- 0.143 |
| PdMo-calc | 6 | 193.84 | 69.1 +- 2.42 (3998) | 0.356 +- 0.012 | 143.75 +- 15.48 (9.75) | 0.742 +- 0.08 |
| | 20 | 646.12 | 74.68 +- 2.47 (3276) | 0.116 +- 0.004 | 116 +- 13.39 (8.64) | 0.18 +- 0.021 |
| | 3 | 92.35 | 63.2 +- 2.47 (4761) | 0.684 +- 0.027 | 162.25 +- 13.44 (10.49) | 1.757 +- 0.146 |
| PdMo-red | 6 | 184.70 | 69.72 +- 2.42 (3918) | 0.377 +- 0.013 | 139 +- 15.13 (9.56) | 0.753 +- 0.082 |
| | 20 | 615.67 | 75.76 +- 2.48 (3136) | 0.123 +- 0.004 | 112.5 +- 13.12 (8.5) | 0.183 +- 0.021 |
| Cu-calc | | Not applicable | 0% (12938) | Not applicable | 0% (4) | Not applicable |
| Ni-calc | | Not applicable | 61.03 +- 2.45 (5042) | Not applicable | 131.75 +- 11.27 (9.27) | Not applicable |
| Fe-calc | | Not applicable | 64.66 +- 2.38 (4572) | Not applicable | 96.75 +- 11.84 (7.87) | Not applicable |
| Co-calc | | Not applicable | 66.05 +- 2.39 (4392) | Not applicable | 66 +- 9.08 (6.64) | Not applicable |
| Mo-calc | | Not applicable | 60.68 +- 2.45 (5087) | Not applicable | 137.25 +- 11.66 (9.49) | Not applicable |
| Cu-red | | Not applicable | 65.19 +- 2.38 (4504) | Not applicable | 97.25 +- 11.89 (7.89) | Not applicable |
| Ni-red | | Not applicable | 67.75 +- 2.4 (4172) | Not applicable | 64 +- 8.88 (6.56) | Not applicable |
| Fe-red | | Not applicable | 54.89 +- 2.41 (5836) | Not applicable | 168.25 +- 13.86 (10.73) | Not applicable |
| Co-red | | Not applicable | 71.22 +- 2.44 (3724) | Not applicable | 160 +- 16.65 (10.4) | Not applicable |
| Mo-red | | Not applicable | 80.52 +- 2.53 (2520) | Not applicable | 110 +- 12.92 (8.4) | Not applicable |

**Table S2:** Concentration, UV/VIS area and RID area for lignin monomer model compounds after injection onto GPC-RID-UV/VIS.

| compound | compound CAS | Conc. (mg/L) | UV/VIS area (a.u.) | RID area (a.u.) |
|---|---|---|---|---|
| Phenol | 108-95-2 | 100 | 4106.0 | 3233.8 |
| Para cresol | 106-44-5 | 100 | 3330.5 | 6189.9 |
| Guaiacol | 90-05-1 | 100 | 4128.4 | 4842.3 |
| Vanillin | 121-33-5 | 100 | 11284.3 | 12940.7 |
| Eugenol | 97-53-0 | 100 | 3287.4 | 9524.8 |
| Isoeugenol | 97-54-1 | 100 | 9856.7 | 15794.3 |
| 3-(4-hydroxyphenyl)-1-propanol | 10210-17-0 | 100 | 2186.9 | 9045.3 |
| Coniferyl alcohol | 458-35-5 | 100 | 6668.7 | 11586.4 |
| Sinapyl alcohol | 20675-96-1 | 100 | 7432.9 | 10076.1 |
| Trans ferulic acid | 537-98-4 | 100 | 7309.8 | 15987.9 |
| 4-Hydroxy-3-methoxycinnamaldehyde | 458-36-6 | 100 | 3170.8 | 18586.2 |
| Vanillin alcohol | 498-00-0 | 100 | 2857.2 | 10741.5 |
| **AVG** | | 100 | 5468.3 | 10712.4 |
| **%RSD (STDEV.S)** | | 100 | 54.5% | 43.3% |

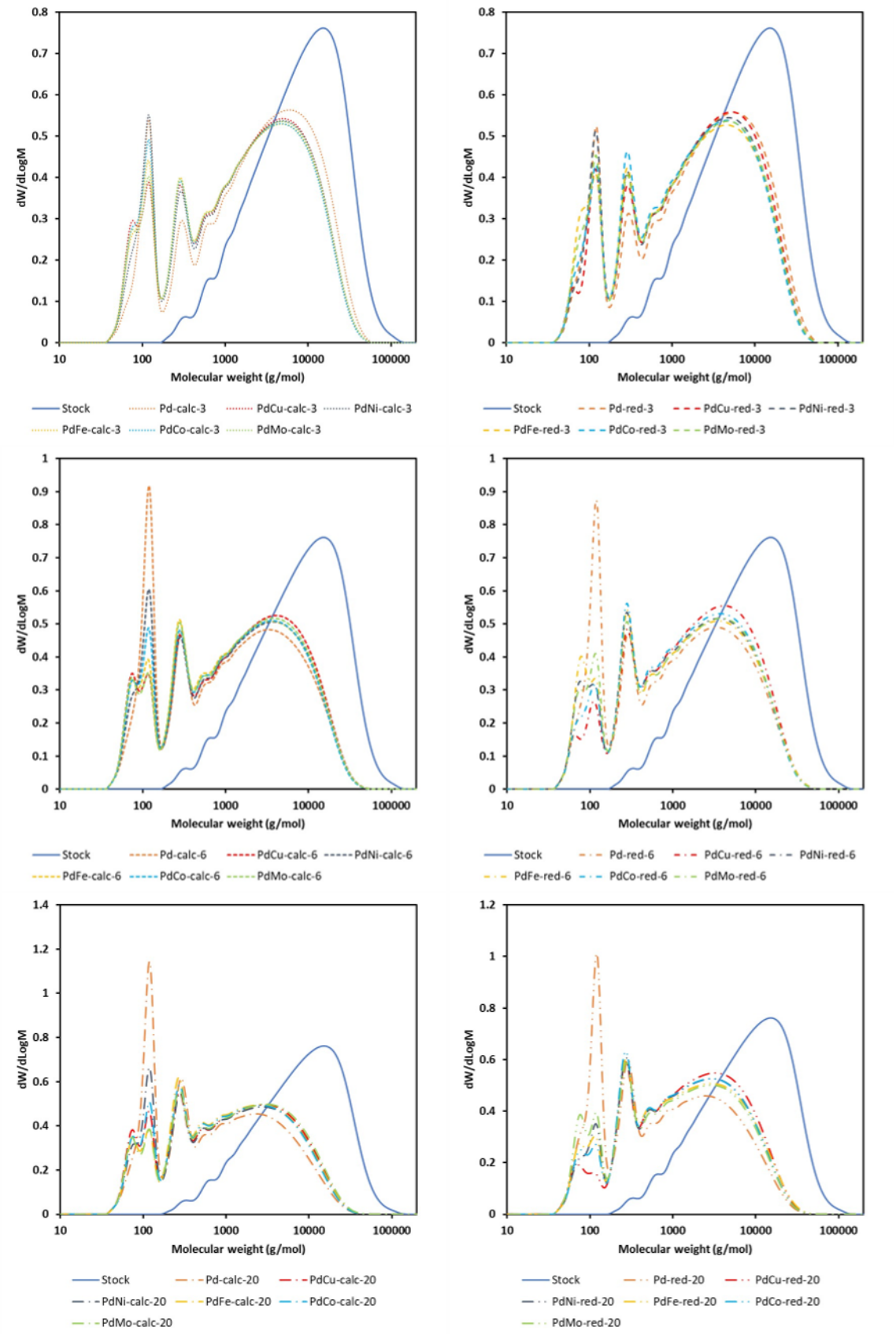


**Figure S4:** Molecular weight distributions, as determined through GPC-RID, for the calcined (left column) and reduced (right column) catalysts at 3 h (top row), 6 h (middle row) and 20 h (bottom row) reaction times.

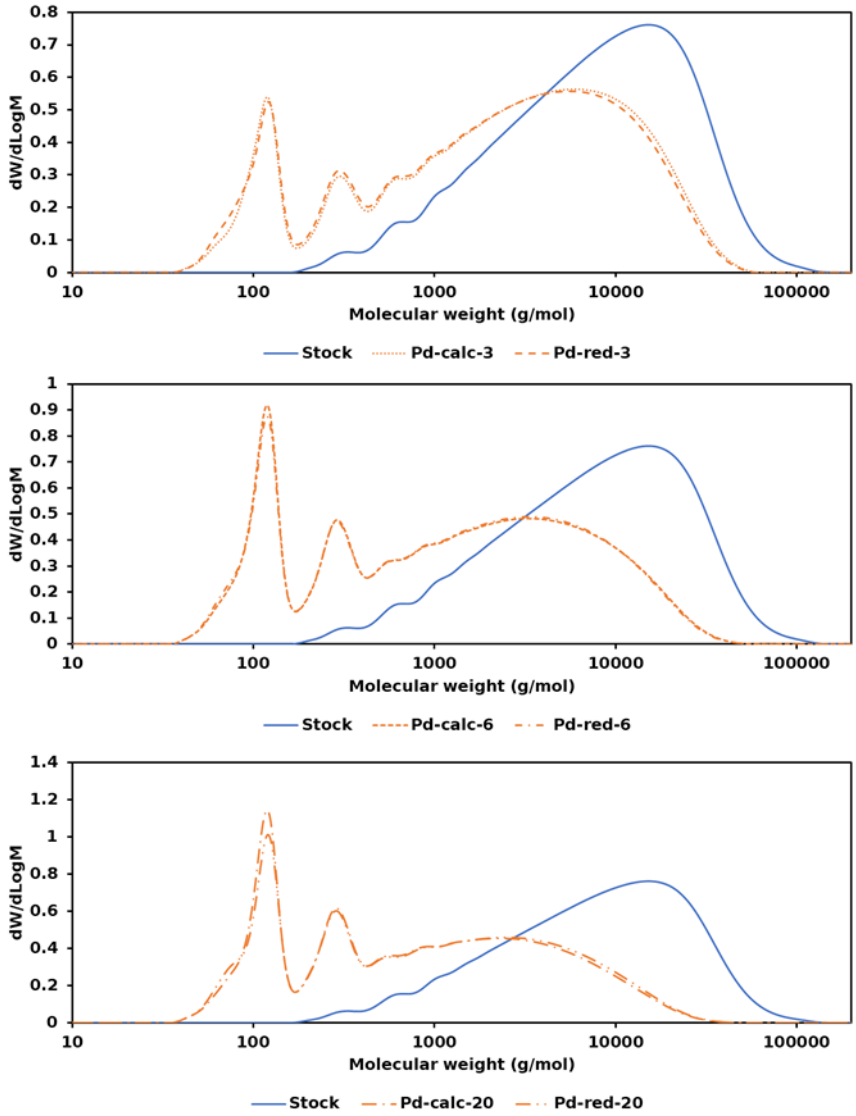


**Figure S5:** Molecular weight distribution, as determined through GPC-RID, for Pd-calc and Pd-red after 2 h (left), 6 h (middle) and 20 h (right) of reaction time.

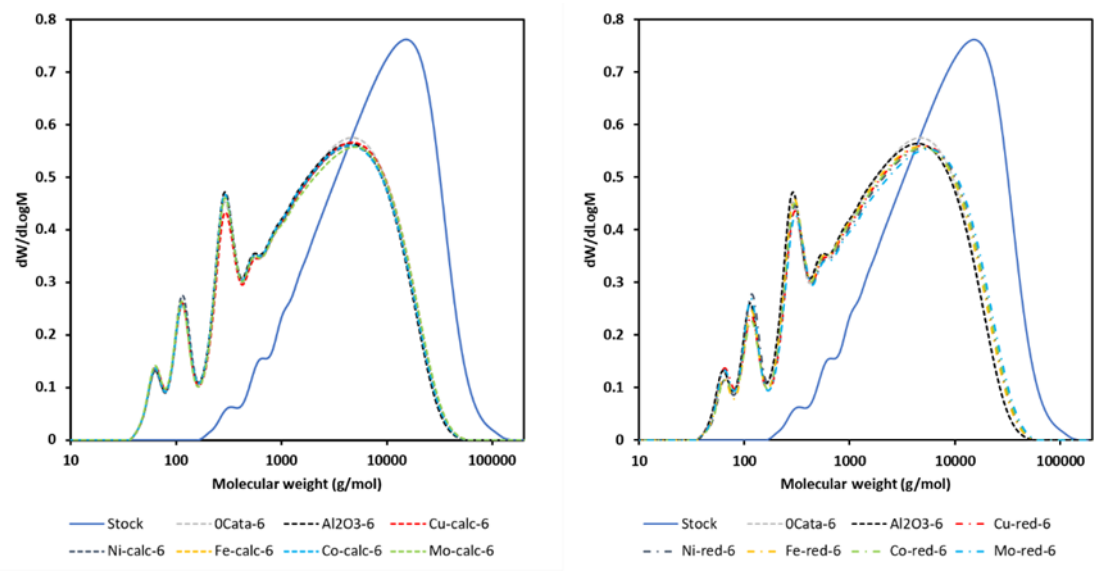


**Figure S6:** Molecular weight distribution, as determined through GPC-RID, for Cu (red), Ni (dark blue), Fe (yellow), Co (light blue) and Mo (green) as the calcined variant (left) and the reduced variant (right), in addition to 0Cata and Al2O3, after 6 h of reaction time.

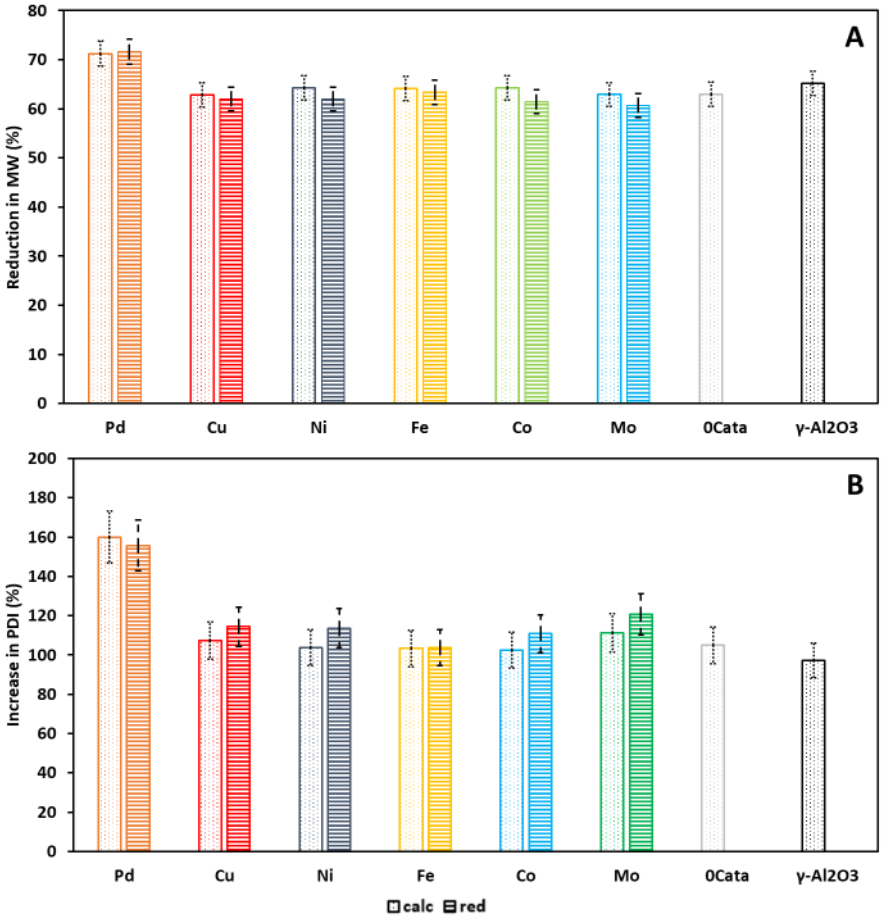


**Figure S7:** Reduction in mass averaged molar mass ($M_W$) (A) and increase in polydispersity index (PDI) (B) for Pd-calc, Cu-calc, Ni-calc, Fe-calc, Co-calc, Mo-calc, Pd-red, Cu-red, Ni-red, Fe-red, Co-red, Mo-red, 0Cata and Al2O3 after 6 h of reaction time. Dotted bars are used for calcined catalysts; striped bars indicate reduced catalysts.

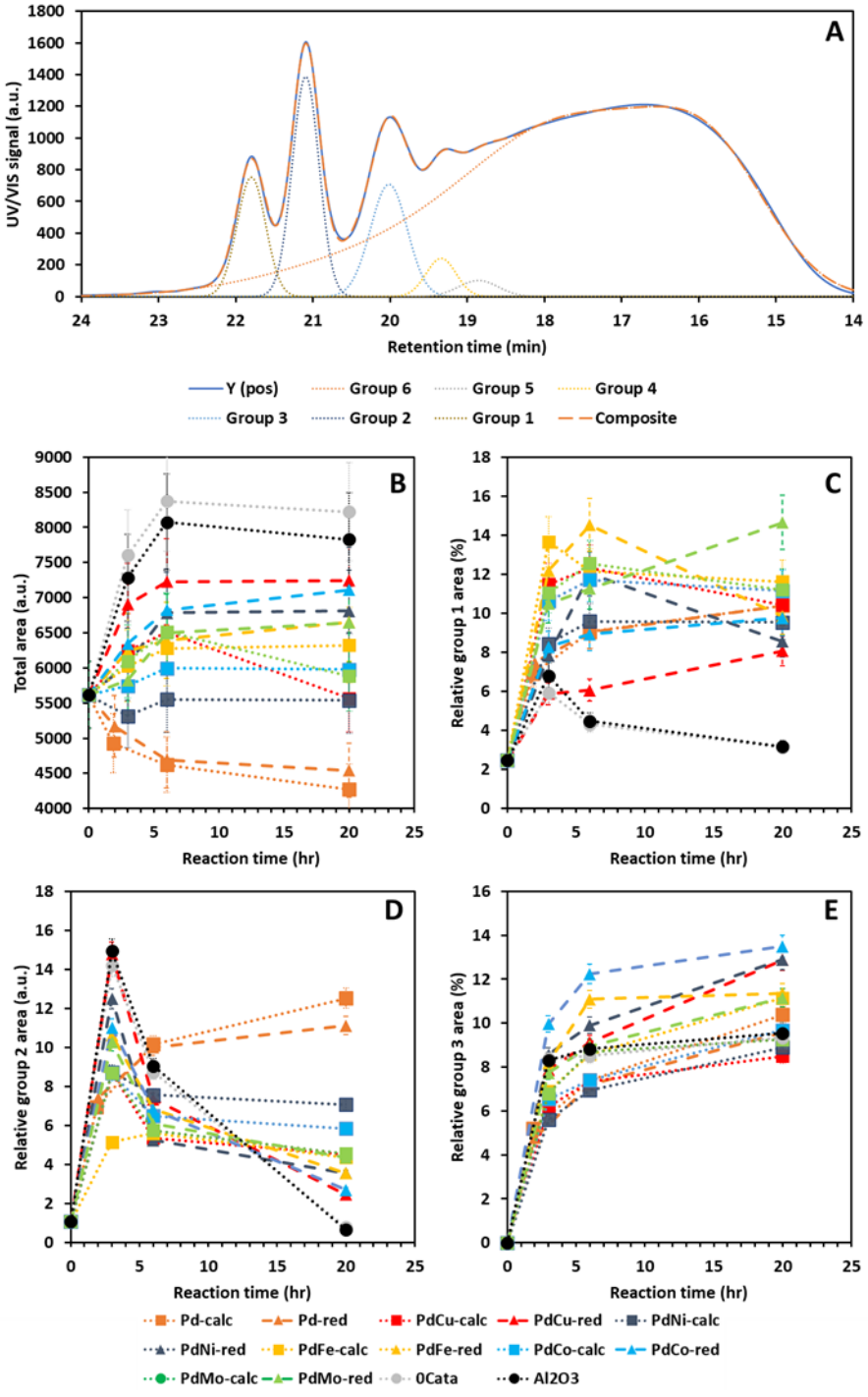


**Figure S8:** Example deconvolution of GPC-UV/VIS chromatogram (A), total surface area under GPC-UV/VIS chromatogram (B) and relative areas for groups 1-3 (C-E), as determined through deconvolution of GPC-UV/VIS, as a function of reaction time for 0Cata, Al2O3 and all Pd(X)-calc/red variations.

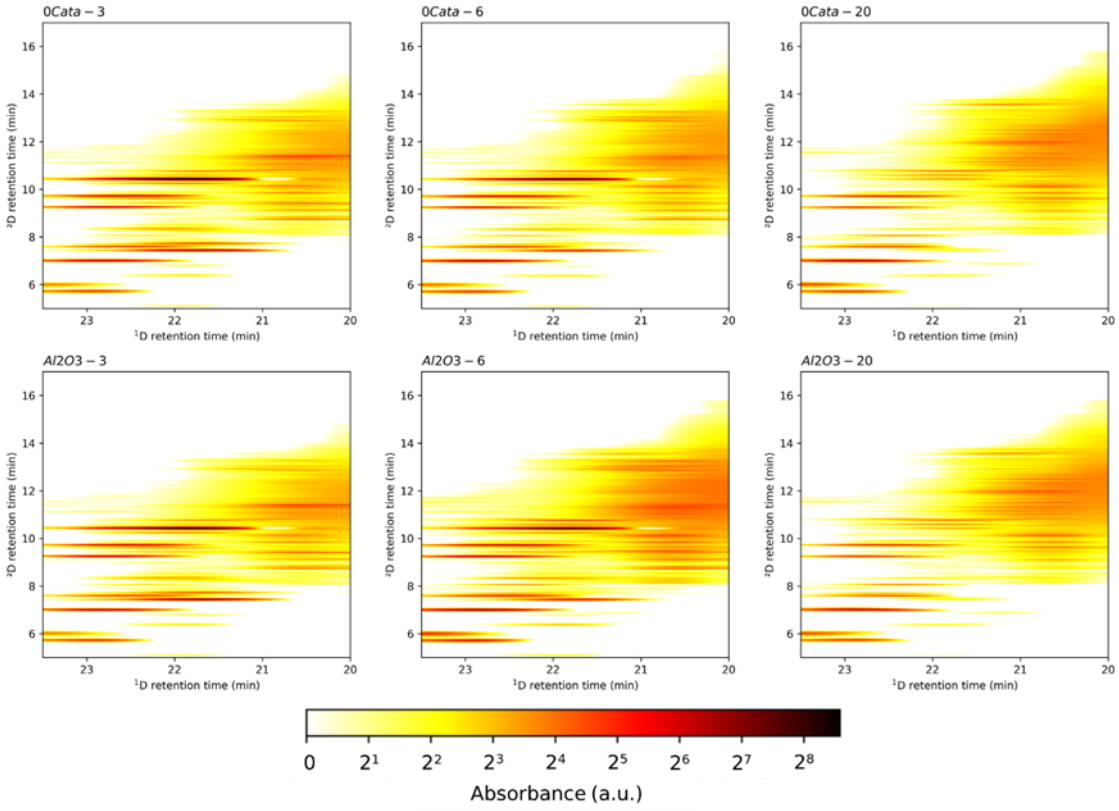


**Figure S9:** GPC-HPLC-UV/VIS heatmaps for the low molecular weight region, i.e., $^{1}t_{R}$ = [20;23.5] min, for the 0cata and Al2O3 variations after 3 h (left column), 6 h (middle column) and 20 h (right column) of reaction time.

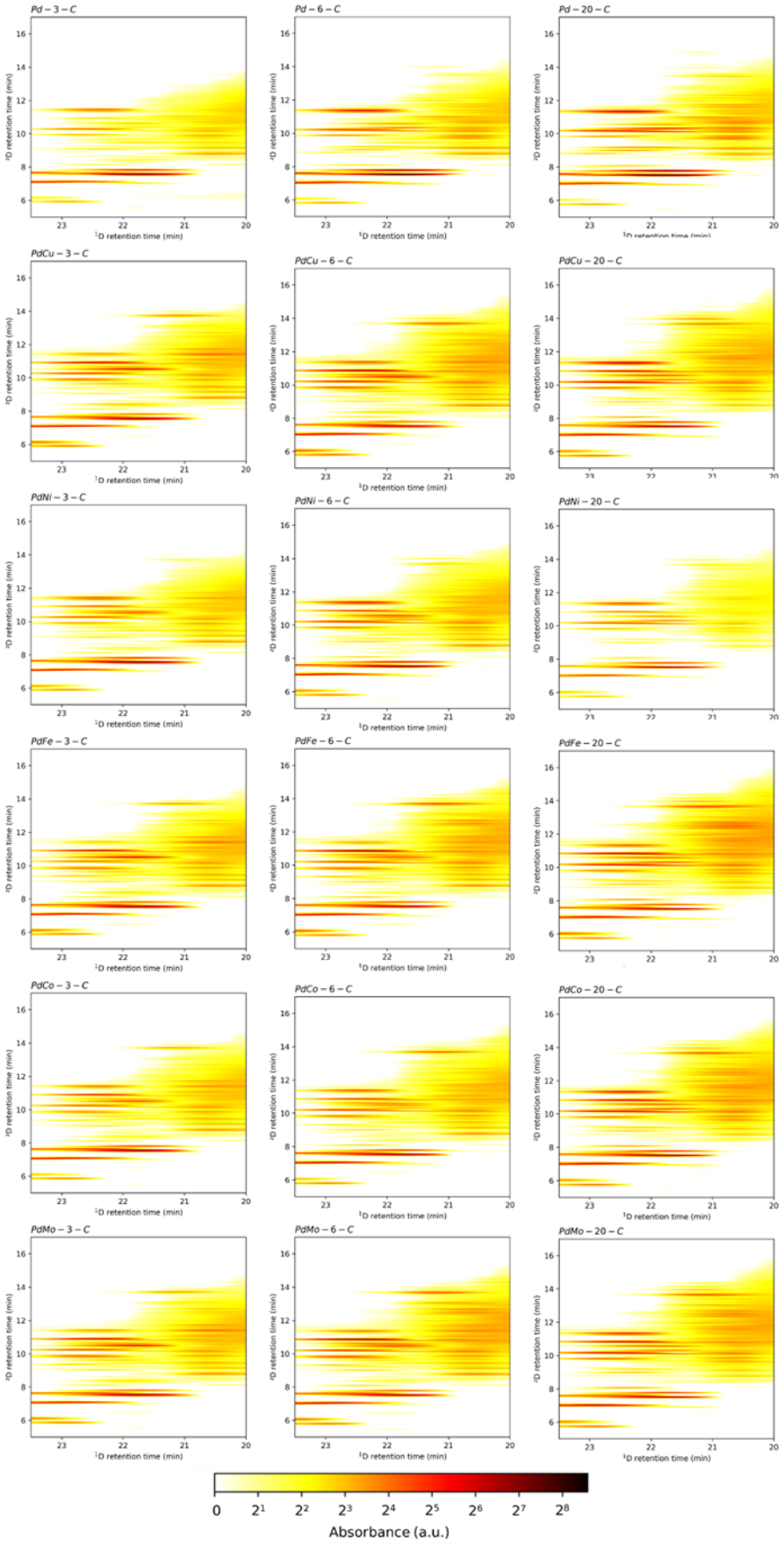


**Figure S10:** GPC-HPLC-UV/VIS heatmaps of the low molecular weight region, i.e., $^{1}t_{R}$ = [20;23.5] min, for the all PdX-calc catalysts at all reaction times.

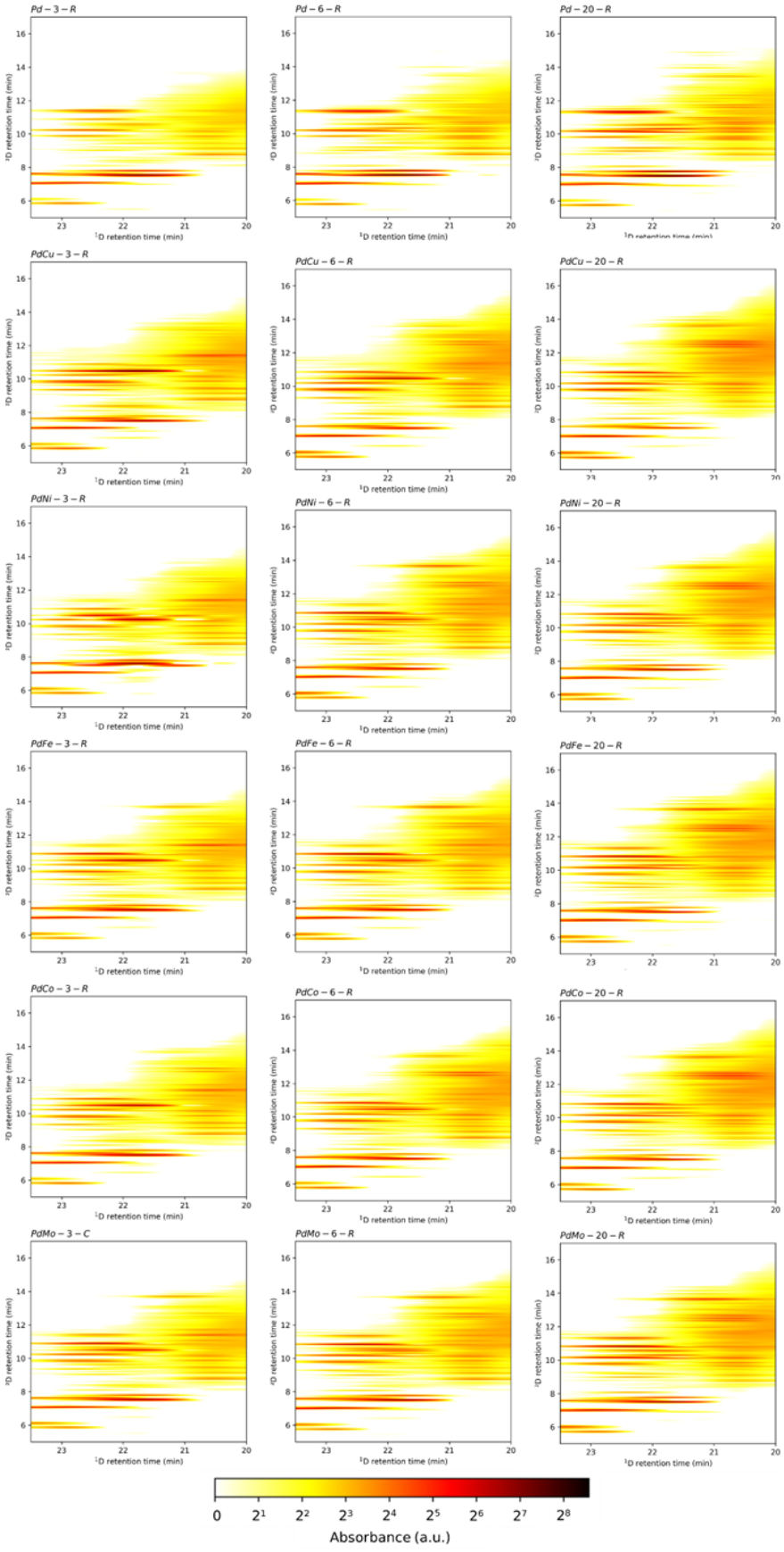


**Figure S11:** GPC-HPLC-UV/VIS heatmaps of the low molecular weight region, i.e., $^{1}t_{R}$ = [20;23.5] min, for the all PdX-red catalysts at all reaction times.

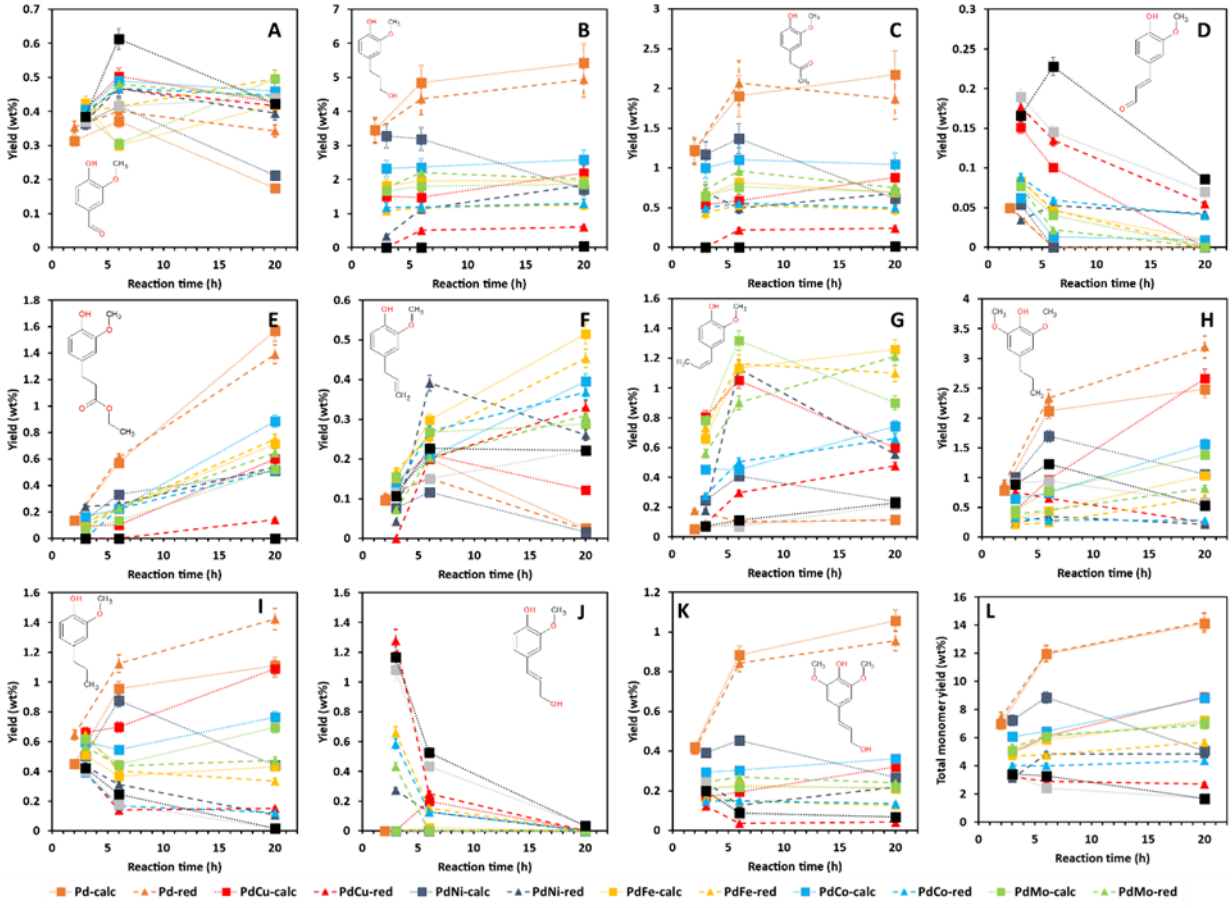


**Figure S12:** Mass yields of V (A), DHCA (B), HMPA (C), HMCA (D), EHF (E), EUG (F), I-EUG (G),4PS (H), MPP (I), CA (J) and SA (K) and the total monomer mass yield as a function of reaction time for 0Cata, Al2O3 and all Pd(X)-calc/red variations.

**Main pathways for cleavage of the β-O-4 linkage**

While the precise reaction mechanisms for each of the linkages within lignin are not fully identified yet in literature, model compound research has provided an indication of the main pathways for cleavage of the β-O-4 linkage, the most abundant linkage in native lignin structures.[1] The monomers identified and quantified within this work can be related to dehydration of the OH group on the alfa carbon (α-C) within the β-O-4 linkage, followed by either hydrogenolysis (route 1.A) or hydrolysis (route 1.B) of the ether linkage between the β-C of the para substitution of one aromatic center and another aromatic center. If hydrogenolysis occurs, an aliphatic double bond is formed between the α-C and β-C of the original β-O-4 linkage, resulting in monomers like isoeugenol (I-EUG), coniferyl alcohol (CA) or sinapyl alcohol (SA), depending on the presence of an aliphatic OH group on the γ-C. This aliphatic double bond can be further hydrogenated under the reductive environment, leading to monomers like 4-propylsyringol (4PS), 2-methoxy-4-propylphenol (MPP), dihydroconiferylalcohol (DHCA) or eugenol (EUG), depending on the presence of an aliphatic OH group on the γ-C and whether this group has undergone dehydration. If route 1.B, i.e., hydrolysis is followed, an aliphatic double bond between the α-C and β-C is formed without removal of the aliphatic OH group on the β-C. The only monomer related to this pathway within this work is 4-hydroxy-3-methoxyphenylacetone (HMPA) wherein the aliphatic double bond is hydrogenated and the aliphatic OH group on the β-C is dehydrogenated.

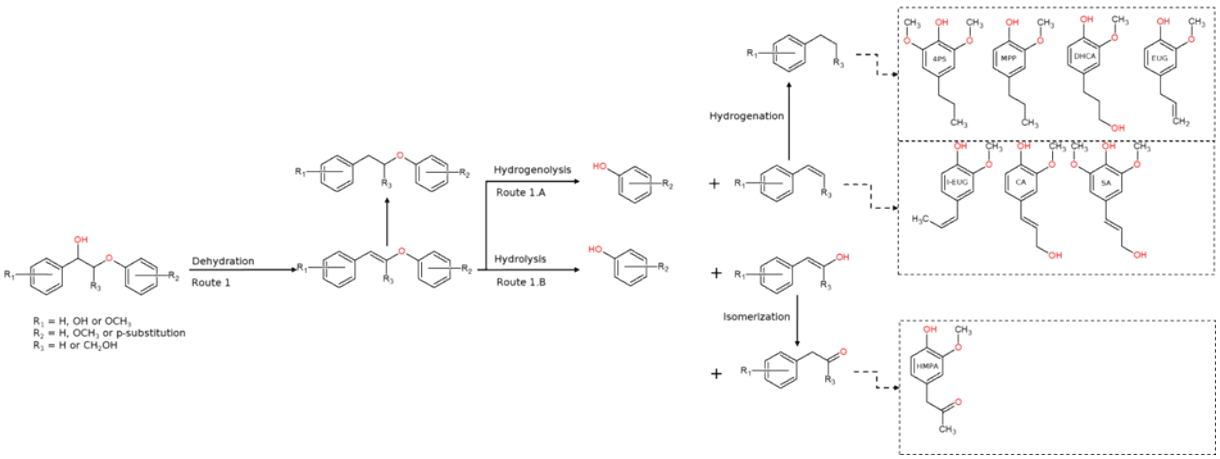


**Figure S13:** Reaction mechanism for the cleavage of a β-O-4 linkage through dehydration and hydrogenolysis or hydrolysis, with indication of 4PS, MPP, DHCA, EUG, I-EUG, CA, SA and HMPA, quantified through GPC-HPLC-UV/VIS analysis.

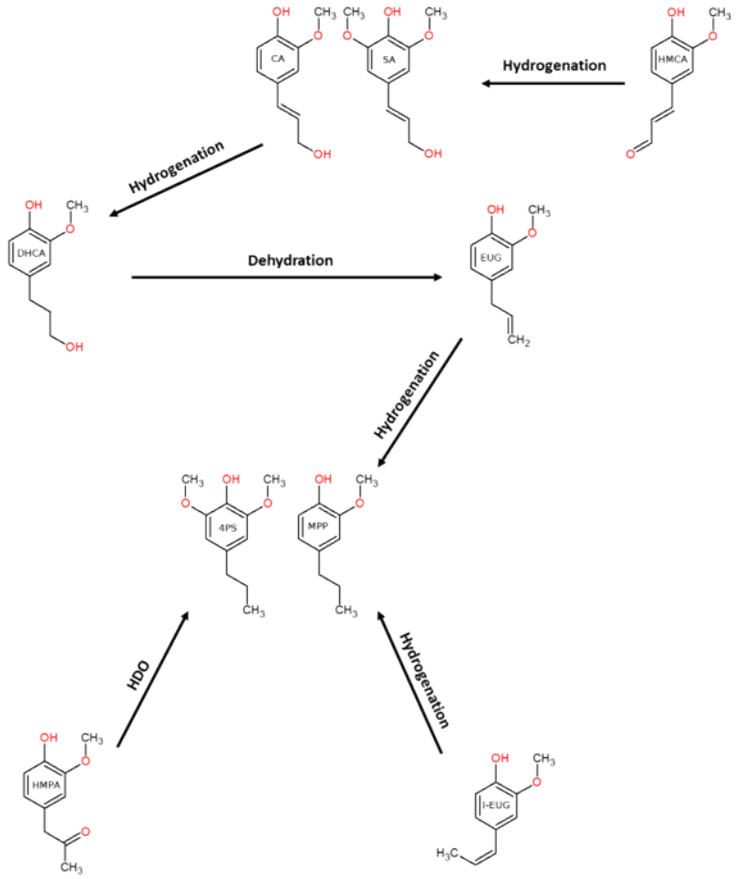


**Figure S14:** Indication of the chemical relationships between the monomeric products quantified through GPC-HPLC-UV/VIS due to hydrodeoxygenation and/or hydrogenation reactions occurring during lignin depolymerization.

[1] B. Zhang, Z. Qi, X. Li, J. Ji, L. Zhang, H. Wang, X. Liu, C. Li, *Green Chemistry* **2019**, *21*, 5556–5564.