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APPENDICES

Appendix A The catalytic activity, 1-hexene selectivity and n-hexane selectivity of low loaded Pd supported on alumina catalyst

Example: Pd-W/Al₂O₃ ratio 1.0

| File name | Peak area | | | Mole of Components | | | %Conv. | %Hexene Selec. |
|-----------|-----------|---------|-----------|--------------------|--------------|--------------|--------|----------------|
| | Reactant | Product | Solvent | Mole Reactant | Mole Product | Mole Solvent | | |
| 1PdW00 | 5594000 | 379790 | 105300292 | 1.77E-07 | 1.40E-08 | 3.32E-06 | 8.14 | 92.41 |
| 1PdW01 | 6107000 | 842327 | 113414111 | 1.62E-07 | 2.73E-08 | 3.58E-06 | 9.62 | 90.23 |
| 1PdW02 | 5517000 | 1202200 | 107414211 | 1.47E-07 | 4.14E-08 | 3.39E-06 | 21.58 | 95.93 |
| 1PdW03 | 5473000 | 1597800 | 101144143 | 1.18E-07 | 6.89E-08 | 3.19E-06 | 27.45 | 89.97 |
| 1PdW04 | 4725000 | 1903000 | 100341198 | 8.56E-08 | 9.80E-08 | 3.17E-06 | 33.11 | 95.23 |
| 1PdW05 | 3900000 | 2696000 | 102478543 | 5.72E-08 | 1.25E-07 | 3.24E-06 | 41.39 | 92.68 |
| 1PdW06 | 3832000 | 3106000 | 104899114 | 3.47E-08 | 1.45E-07 | 3.31E-06 | 43.54 | 93.15 |
| 1PdW07 | 2675000 | 2849000 | 112345099 | 1.96E-08 | 1.60E-07 | 3.55E-06 | 48.53 | 87.34 |
| 1PdW08 | 2791000 | 3847000 | 98851424 | 1.01E-08 | 1.68E-07 | 3.12E-06 | 53.38 | 97.39 |
| 1PdW09 | 2231432 | 4218000 | 107421098 | 4.90E-09 | 1.73E-07 | 3.39E-06 | 55.71 | 92.67 |
| 1PdW10 | 1664000 | 4079000 | 100125199 | 2.17E-09 | 1.75E-07 | 3.16E-06 | 60.69 | 88.52 |
| 1PdW11 | 1035000 | 3111000 | 109834115 | 8.53E-10 | 1.76E-07 | 3.47E-06 | 66.51 | 90.66 |
| 1PdW12 | 1258000 | 5100000 | 101114555 | 3.03E-10 | 1.77E-07 | 3.19E-06 | 76.45 | 92.44 |
| 1PdW13 | 933860 | 5623000 | 100055489 | 7.13E-11 | 1.77E-07 | 3.16E-06 | 81.42 | 96.87 |
| 1PdW14 | 498948 | 5458000 | 99988443 | 1.33E-11 | 1.77E-07 | 3.16E-06 | 85.14 | 92.32 |
| 1PdW15 | 326578 | 5958100 | 104097773 | 2.23E-12 | 1.78E-07 | 3.29E-06 | 100.00 | 97.98 |

Calculation: At File name 1PdW12

$$\text{Sol}^n \quad \text{From } 1\text{-Hexyne conversion } (\%1\text{-Hy}_{\text{conv}}) = \frac{(\text{moles of } 1\text{-Hy}_{\text{initial}} - \text{moles of } 1\text{-Hy}_{\text{final}})}{\text{moles of } 1\text{-Hy}_{\text{initial}}} \times 100$$
$$= \frac{(3.0281 \times 10^{-10} - 7.131 \times 10^{-11})}{3.0281 \times 10^{-10}} \times 100$$
$$= 76.45 \%$$

$$\text{From } 1\text{-Hexene selectivity } (\%1\text{-Hexene}_{\text{sel}}) = \frac{(\text{moles of } 1\text{-He}_{\text{final}} - \text{moles of } 1\text{-He}_{\text{initial}})}{\text{moles of } 1\text{-Hy converted}} \times 100$$
$$= \frac{(1.77138 \times 10^{-7} - 1.76924 \times 10^{-7})}{(3.0281 \times 10^{-10} - 7.131 \times 10^{-11})} \times 100$$
$$= 92.44 \%$$

So, file name 1PdW12 shows 1-Hexyne conversion ($\%1\text{-Hy}_{\text{conv}}$) = 76.45 % and 1-Hexene selectivity ($\%1\text{-Hexene}_{\text{sel}}$) = 92.44 %

Table A1 The catalytic activity, 1-hexene selectivity and n-hexane selectivity of 0.3%Pd supported on alumina catalyst

| 0.3%Pd | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|--------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 0.22 | 5.57 | 15.42 | 26.03 | 43.18 | 61.11 | 100.00 |
| 1-Hexene selectivity (%) | 38.75 | 45.31 | 52.67 | 56.21 | 57.84 | 59.85 | 65.62 |
| n-Hexane selectivity (%) | 3.86 | 4.62 | 5.15 | 6.74 | 9.54 | 13.56 | 28.74 |

Appendix B The catalytic activity, 1-hexene selectivity and n-hexane selectivity of Pd-Cu supported on alumina catalysts

Table B1 The catalytic activity, 1-hexene selectivity and n-hexane selectivity of Pd-Cu with Pd/Cu ratio of 0.25

| Pd-Cu ratio 0.25 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 0.22 | 2.43 | 3.56 | 6.42 | 9.06 | 12.76 | 16.42 |
| 1-Hexene selectivity (%) | 7.68 | 8.54 | 9.32 | 12.52 | 16.12 | 18.98 | 20.47 |
| n-Hexane selectivity (%) | 14.63 | 15.61 | 15.54 | 18.61 | 21.94 | 28.51 | 34.85 |

Table B2 The catalytic activity, 1-hexene selectivity and n-hexane selectivity of Pd-Cu with Pd/Cu ratio of 0.5

| Pd-Cu ratio 0.5 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 0.27 | 4.58 | 11.04 | 13.14 | 13.67 | 18.23 | 26.32 |
| 1-Hexene selectivity (%) | 11.57 | 14.13 | 21.42 | 23.45 | 24.64 | 27.04 | 27.45 |
| n-Hexane selectivity (%) | 12.61 | 13.61 | 13.55 | 16.15 | 19.85 | 26.95 | 32.52 |

Table B3 The catalytic activity, 1-hexene selectivity and n-hexane selectivity of Pd-Cu with Pd/Cu ratio of 1.0

| Pd-Cu ratio 1.0 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 0.39 | 5.41 | 5.77 | 12.15 | 23.08 | 24.62 | 30.25 |
| 1-Hexene selectivity (%) | 15.32 | 19.53 | 24.99 | 28.24 | 29.74 | 30.23 | 30.56 |
| n-Hexane selectivity (%) | 10.51 | 11.56 | 11.56 | 14.21 | 17.12 | 24.73 | 30.14 |

Table B4 The catalytic activity, 1-hexene selectivity and n-hexane selectivity of Pd-Cu with Pd/Cu ratio of 1.5

| Pd-Cu ratio 1.5 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 0.46 | 3.10 | 7.56 | 14.13 | 23.37 | 28.83 | 37.08 |
| 1-Hexene selectivity (%) | 20.13 | 23.24 | 26.21 | 31.13 | 34.12 | 37.52 | 37.24 |
| n-Hexane selectivity (%) | 8.42 | 9.03 | 9.51 | 12.51 | 15.73 | 22.93 | 28.21 |

Table B5 The catalytic activity, 1-hexene selectivity and n-hexane selectivity of Pd-Cu with Pd/Cu ratio of 2.0

| Pd-Cu ratio 2.0 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 0.67 | 5.67 | 5.65 | 20.12 | 24.77 | 45.04 | 48.11 |
| 1-Hexene selectivity (%) | 29.42 | 32.01 | 40.25 | 42.13 | 44.43 | 46.94 | 46.34 |
| n-Hexane selectivity (%) | 6.41 | 7.25 | 7.56 | 10.25 | 13.25 | 20.14 | 26.83 |

Appendix C The catalytic activity and 1-hexene selectivity of Pd-W supported on alumina catalysts

Table C1 The catalytic activity and 1-hexene selectivity of Pd-W with Pd/W ratio of 0.25

| Pd-W ratio 0.25 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|--------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 8.45 | 30.68 | 46.43 | 60.25 | 77.95 | 95.99 | 100.00 |
| 1-Hexene selectivity (%) | 90.14 | 89.53 | 83.25 | 82.98 | 86.48 | 82.26 | 88.05 |

Table C2 The catalytic activity and 1-hexene selectivity of Pd-W with Pd/W ratio of 0.5

| Pd-W ratio 0.5 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|--------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 5.88 | 11.14 | 19.57 | 32.87 | 48.53 | 67.52 | 100.00 |
| 1-Hexene selectivity (%) | 90.08 | 90.52 | 81.25 | 78.98 | 89.20 | 83.45 | 78.69 |

Table C3 The catalytic activity and 1-hexene selectivity of Pd-W with Pd/W ratio of 1.0

| Pd-W ratio 1.0 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|--------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 7.96 | 21.58 | 41.39 | 53.38 | 66.51 | 85.14 | 100.00 |
| 1-Hexene selectivity (%) | 93.21 | 97.93 | 92.68 | 97.39 | 90.66 | 92.32 | 97.98 |

Table C4 The catalytic activity and 1-hexene selectivity of Pd-W with Pd/W ratio of 1.5

| Pd-W ratio 1.5 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|--------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 7.02 | 22.58 | 33.20 | 43.86 | 58.63 | 86.13 | 100.00 |
| 1-Hexene selectivity (%) | 91.99 | 89.40 | 83.24 | 79.39 | 78.22 | 87.45 | 86.28 |

Table C5 The catalytic activity and 1-hexene selectivity of Pd-W with Pd/W ratio of 2.0

| Pd-W ratio 2.0 | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|--------|
| Reaction time (h) | 0.5 | 3 | 6 | 9 | 12 | 15 | 18 |
| 1-Hexyne conversion (%) | 6.69 | 11.91 | 22.57 | 36.52 | 54.53 | 83.13 | 100.00 |
| 1-Hexene selectivity (%) | 91.87 | 89.51 | 89.29 | 86.98 | 86.08 | 83.45 | 80.69 |

Appendix D Atomic Absorption Spectroscopy (Varian) Results

Example: from Table D1, 0.3% Pd = 2.70 ppm, weight = 0.096

Calculation: %Metal = $\frac{\{\text{Conc.} \left(\frac{\text{g}}{\text{ml}} \right) (100\text{ml})\}}{\text{gCatalyst}} \times 100$

Solⁿ From %Metal = $\frac{\{\text{Conc.} \left(\frac{\text{g}}{\text{ml}} \right) (100\text{ml})\}}{\text{gCatalyst}} \times 100$

$$\begin{aligned} \text{ %Metal} &= \frac{2.70 \times 10^{-6} \times 100}{0.096} \times 100 \\ &= 0.28 \text{ %Pd} \end{aligned}$$

So, the amount of 0.3%Pd supported on Alumina catalyst, analyzed by AAS, equals 0.28%

Table D1 Low loaded Pd supported on alumina catalyst

| Pd Results | | | | |
|------------|------------|-------|---------|------|
| Sample | Conc (ppm) | Wt(g) | Factor | % Pd |
| Pd | 2.70 | 0.096 | 1041.67 | 0.28 |

Table D2 Pd-Cu supported on alumina catalysts

| Pd Results | | | | |
|------------|------------|-------|---------|------|
| Sample | Conc (ppm) | Wt(g) | Factor | % Pd |
| Pd 0.25 | 1.8 | 0.114 | 1754.38 | 0.32 |
| Pd 0.5 | 3.43 | 0.109 | 915.75 | 0.31 |
| Pd 1.0 | 3.72 | 0.109 | 917.43 | 0.34 |
| Pd 1.5 | 3.24 | 0.108 | 919.96 | 0.30 |
| Pd 2.0 | 3.56 | 0.114 | 873.36 | 0.31 |

| Cu Results | | | | |
|------------|------------|-------|---------|------|
| Sample | Conc (ppm) | Wt(g) | Factor | % Cu |
| Cu 0.25 | 4.13 | 0.114 | 1754.39 | 0.72 |
| Cu 0.5 | 4.23 | 0.109 | 915.75 | 0.39 |
| Cu 1.0 | 2.07 | 0.109 | 917.43 | 0.19 |
| Cu 1.5 | 1.50 | 0.109 | 919.96 | 0.14 |
| Cu 2.0 | 1.07 | 0.115 | 873.36 | 0.09 |

Table D3 Pd-W supported on alumina catalysts

| Pd Results | | | | |
|------------|------------|-------|--------|------|
| Sample | Conc (ppm) | Wt(g) | Factor | % Pd |
| Pd 0.25 | 2.88 | 0.113 | 882.61 | 0.25 |
| Pd 0.5 | 2.59 | 0.107 | 934.58 | 0.24 |
| Pd 1.0 | 4.06 | 0.110 | 908.27 | 0.37 |
| Pd 1.5 | 2.96 | 0.113 | 881.83 | 0.26 |
| Pd 2.0 | 2.49 | 0.105 | 952.38 | 0.24 |

| W Results | | | | |
|-----------|------------|-------|--------|------|
| Sample | Conc (ppm) | Wt(g) | Factor | % W |
| W 0.25 | 32.00 | 0.113 | 882.61 | 2.82 |
| W 0.5 | 18.33 | 0.107 | 934.58 | 1.71 |
| W 1.0 | 10.67 | 0.110 | 908.27 | 0.97 |
| W 1.5 | 9.00 | 0.113 | 881.83 | 0.79 |
| W 2.0 | 6.33 | 0.105 | 952.38 | 0.60 |

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