**Supplementary Materials**

Catalytic Oxidation of Benzyl Alcohol using Nanosized Ni/Cu Schiff-Base Complexes and their Metal Oxides Nanoparticles

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**Table S1.** Physical and analytical properties of the ligands and their respective complexes

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***μ*eff†**  **B.M.** | **Conductance**  **Λm (Ω-1 cm2**  **mol-1)** | **Elemental analysis**  **found (calculated)** | | | **(M. F)**  **M.wt** | **M.p. (°C)** | **Color** | **Com.** |
| N | H | C |
| - | 3.67 | 10.76  (11.47) | 4.61  (4.91) | 60.00  (63.93) | (C13H12O3N2)  244 | 250 | Orange | ahpv |
| - | 6.80 | 17.28  (17.32) | 3.70  (3.74) | 59.25  (59.21) | (C12H9O3N3)  243 | 245 | Brown | ahpnb |
| 2.07 | 6.75 | 8.19  (8.05) | 4.09  (4.22) | 45.68  (45.53) | (C13H18O7N2Cu)  377.5 | >300 | Light green | ahpvCu |
| 2.50 | 8.87 | 13.55  (13.49) | 3.87  (3.79) | 46.48  (46.35) | (C24H24O10N6Cu)  619.5 | >300 | Brick red | ahpnbCu |
| 3.69 | 4.76 | 7.51  (7.65) | 4.82  (4.73) | 41.85  (41.77) | (C13H18O7N2Ni)  372.7 | >300 | Brown | ahpvNi |

**†** Magnetic moment (in Bohr Magneton)

**Table S2.** Infrared spectral bands of the Schiff-base ligands and their complexes

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| ***υ*(M–N)** | ***υ*(M–O)** | ***υ*(H2O)**  **coord** | ***υ*(C–O)**  **ph** | ***υ*(C=N)** | ***υ*(CH)**  **ar** | ***υ*(OH/**  **H2O)**1 | **Compound** |
| - | - | - | 1307(m) | 1613(s) | 3060(w) | 3447(w) | ahpv |
| - | - | - | 1288(m) | 1621(s) | 3100(w) | 3475(w) | ahpnb |
| 535(m) | 736(m) | 975(m) | 1298(m) | 1608(s) | 3047(w) | 3450(w) | ahpvCu |
| 656(w) | 723(w) | 814(w) | 1286(w) | 1614(s) | 3079(w) | 3490(w) | ahpnbCu |
| 527(m) | 733(s) | 976(m) | 1272(m) | 1601(s) | 3051(w) | 3450(w) | ahpvNi |

1 s: strong, m: medium, w: weak, ar: aromatic, ph: phenolic, coord: coordinated water.

**Table S3.** Thermal analysis data for the Schiff-base metal complexes\*.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Weight loss (%) | | Lost fragment | Degradation  temperature (°C) | Complex |
| Found | Theoretical |
| 5.11 | 5.27 | H2O | 36–155 | ahpvCu |
| 27.54 | 27.81 | H2O + C5H3N | 155–391 |
| 48.41 | 48.31 | C8H7NO3 | 391–501 |
| 18.94 | 18.61 | Residue Cu | >501 |
| 6.55 | 5.81 | 2H2O | 34–165 | ahpnbCu |
| 12.56 | 13.23 | 2H2O + NO2 | 165–243 |
| 50.21 | 51.49 | C17H11N4O3 | 243–310 |
| 19.66 | 19.20 | C7H5NO | 310–409 |
| 11.02 | 10.27 | Residue Cu | >409 |
| 4.78 | 4.82 | H2O | 14–166 | ahpvNi |
| 22.91 | 22.80 | 3H2O,OCH3 | 166–325 |
| 31.51 | 31.66 | C7H4ON | 325–398 |
| 24.83 | 24.95 | C5H3NO | 398–479 |
| 15.97 | 15.77 | Residue Ni | >479 |

\*Thermogravimetric tests were carried out under N2 at a heating rate of 10 °C min-1

**Table S4**. Oxidation of benzyl alcohol (BzOH) catalyzed by the ahpvCu complex using aqueous H2O2 in DMSO.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Entrya | Temp. (°C) | Time (h) | Yield (%)b | | | | Conversion  (%) | Selectivity  (%) |
| BzHb | BzAc | Side  products | Ra |
| 1 | 60 | 0.5 | 32 | 0 | 0 | 68 | 32 | 100 |
| 2 | 1 | 51 | 0 | 0 | 49 | 51 | 100 |
| 3 | 2 | 71 | 0 | 0 | 29 | 71 | 100 |
| 4 | 4 | 70 | 14 | 0 | 16 | 84 | 83 |
| 5 | 70 | 0.5 | 55 | 0 | 0 | 45 | 55 | 100 |
| 6 | 1 | 77 | 0 | 0 | 23 | 77 | 100 |
| 7 | 2 | 95 | 0 | 0 | 5 | 95 | 100 |
| 8 | 4 | 93 | 3 | 0 | 4 | 96 | 97 |
| 9 | 80 | 0.5 | 80 | 0 | 0 | 20 | 80 | 100 |
| 10 | 1 | 74 | 11 | 0 | 15 | 85 | 87 |
| 11 | 2 | 73 | 14 | 0 | 13 | 87 | 84 |
| 12 | 4 | 70 | 13 | 6 | 11 | 89 | 79 |
| 13 | 90 | 0.5 | 75 | 0 | 0 | 25 | 75 | 100 |
| 14 | 1 | 86 | 2 | 0 | 12 | 88 | 98 |
| 15 | 2 | 85 | 7 | 0 | 8 | 92 | 92 |
| 16 | 4 | 82 | 11 | 0 | 7 | 93 | 88 |

a Oxidation of benzyl alcohol (R) (1.0 mmol) catalyzed by ahpvCu complex (0.03 mmol) with aqueous H2O2(3.00 mmol) in 10 cm3 DMSO for 0.5–4 h.

b Yield based on GC results: selectivity percentage of the target oxide product, benzaldehyde (BzH), and the other

product, benzoic acid (BzA).

c The side product was mainly benzoic acid (BzA).

**Table S5.** Oxidation of benzyl alcohol (BzOH) catalyzed by CuO using aqueous H2O2 in DMSO

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Entrya | Temp. (°C) | Time (h) | Yield (%)b | | | | Conversion  (%) | Selectivity  (%) |
| BzHb | BzAc | Side  products | Ra |
| 1 | 60 | 0.5 | 45 | 0 | 0 | 55 | 45 | 100 |
| 2 | 1 | 53 | 0 | 0 | 47 | 53 | 100 |
| 3 | 2 | 63 | 5 | 0 | 32 | 68 | 93 |
| 4 | 4 | 67 | 10 | 0 | 23 | 77 | 87 |
| 5 | 70 | 0.5 | 59 | 0 | 0 | 41 | 59 | 100 |
| 6 | 1 | 79 | 0 | 0 | 21 | 79 | 100 |
| 7 | 2 | 98 | 0 | 0 | 2 | 98 | 100 |
| 8 | 4 | 98 | 2 | 0 | 0 | 100 | 98 |
| 9 | 80 | 0.5 | 76 | 0 | 0 | 24 | 76 | 100 |
| 10 | 1 | 79 | 11 | 0 | 10 | 90 | 88 |
| 11 | 2 | 78 | 20 | 0 | 2 | 98 | 80 |
| 12 | 4 | 77 | 22 | 0 | 1 | 99 | 78 |
| 13 | 90 | 0.5 | 88 | 0 | 0 | 12 | 88 | 100 |
| 14 | 1 | 85 | 7 | 0 | 8 | 92 | 92 |
| 15 | 2 | 83 | 11 | 0 | 6 | 94 | 88 |
| 16 | 4 | 84 | 15 | 0 | 1 | 99 | 85 |

a Oxidation of benzyl alcohol (R) (1.0 mmol) catalyzed by ahpvCu complex (0.03 mmol) with aqueous H2O2(3.00 mmol) in 10 cm3 DMSO for 0.5–4 h.

b Yield based on GC results: selectivity percentage of the target oxide product, benzaldehyde (BzH), and the other

product, benzoic acid (BzA).

c The side product was mainly benzoic acid (BzA).

**Table S6**. Oxidation of benzyl alcohol (BzOH) catalyzed by different concentrations of catalysts using aqueous H2O2 in acetonitrile

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Compound | Complex  conc.  mmol | Temp  (°C) | Time  (h) |  | Yield (%) | | | Conversion (%) | Selectivity (%) |
| BzH | BzA | Side  products | R |
| ahpvCu | 0.01 | 70 | 2 | 36 | 0 | 0 | 64 | 36 | 100 |
| 0.02 | 78 | 0 | 0 | 22 | 78 | 100 |
| 0.03 | 95 | 0 | 0 | 5 | 95 | 100 |
| 0.04 | 85 | 13 | 0 | 2 | 98 | 87 |
| ahpnbCu | 0.01 | 70 | 2 | 45 | 0 | 0 | 55 | 45 | 100 |
| 0.02 | 71 | 0 | 0 | 29 | 71 | 100 |
| 0.03 | 94 | 0 | 0 | 6 | 94 | 100 |
| 0.04 | 93 | 6 | 0 | 1 | 99 | 94 |
| ahpvNi | 0.01 | 70 | 1 | 31 | 0 | 0 | 69 | 31 | 100 |
| 0.02 | 49 | 0 | 0 | 51 | 49 | 100 |
| 0.03 | 55 | 0 | 0 | 45 | 55 | 100 |
| 0.04 | 51 | 20 | 0 | 29 | 71 | 72 |
| CuO | 0.01 | 70 | 2 | 55 | 0 | 0 | 45 | 55 | 100 |
| 0.02 | 80 | 0 | 0 | 20 | 80 | 100 |
| 0.03 | 98 | 0 | 0 | 2 | 98 | 100 |
| 0.04 | 91 | 8 | 1 | 0 | 100 | 91 |
| NiO | 0.01 | 70 | 1 | 46 | 0 | 0 | 44 | 46 | 100 |
| 0.02 | 78 | 0 | 0 | 22 | 78 | 100 |
| 0.03 | 97 | 0 | 0 | 3 | 97 | 100 |
| 0.04 | 89 | 8 | 2 | 1 | 99 | 90 |



**Figure S1.** Electronic spectra for the ahpvCu complex and its components in DMF at 298 K (ahp = 2-amino-3-hydroxypyridine, v = 3-methoxysalicylaldehyde).



**Figure S2.** pH-profiles of the designated complexes in aqueous-ethanol mixture at [M] = [L] = 1 × 10-3 M and 298 K.

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** | **(d)** |

**Figure S3.** (a) and (b) are TEM images of CuO and NiO; (c) and (d) are their calculated histograms.



**Fig. S4-A.** Electronic spectra for the ahpvCu complex in the absence and presence of aqueous H2O2 in DMSO at 70 °C



**Fig. S4-B.** Electronic spectra for the ahpnbCu complex in the absence and presence of aqueous H2O2 in DMSO at 70 °C



**Fig. S5-A.** Repetitive electronic spectral scans for the ahpnbCu complex with benzyl alcohol in the presence of aqueous H2O2 in DMSO at 70 °C at time intervals of 20 min



**Figure S5-B.** Repetitive electronic spectral scans for the ahpvCu complex with benzyl alcohol in the presence of aqueous H2O2 in DMSO at 70 °C at time intervals of 20 min

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**Scheme S1.** Proposed structures for the ahpvCu, ahpvNi, and ahpnbCu complexes.



**Scheme 2.** Synthesis of ahpv and ahpnb ligands, where ahp = 2-amino-3-hydroxypyridine, nb = 4-nitrobenzaldehyde, and v = 3-methoxysalicylaldehyde.