Supplementary Information

(a) (b)

Figure: S1 Catalyst synthesis process (a) Fehling's route of catalyst preparation via glucose oxidation assisted precipitation (b) Conventional co-precipitation method using jacketed reactor.

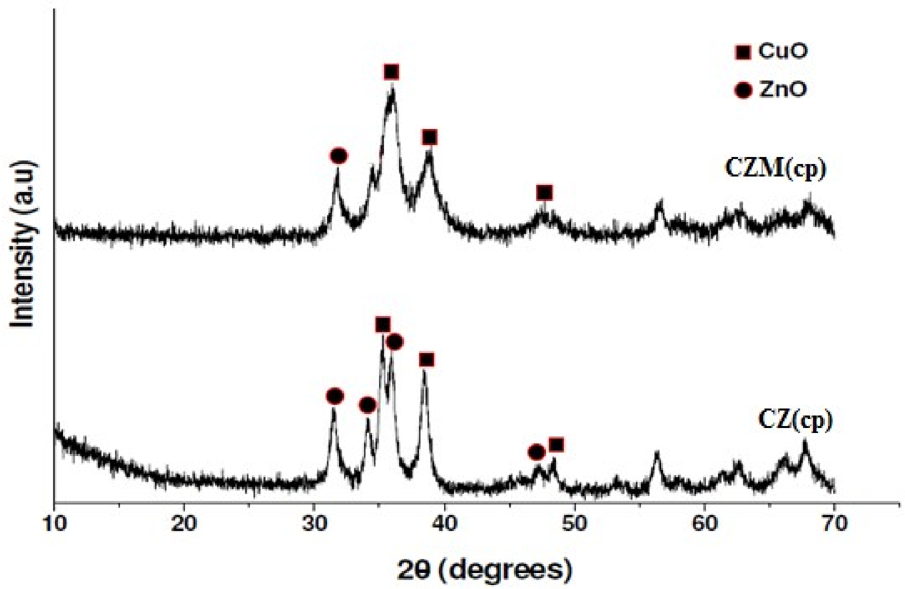


Figure: S2 XRD pattern of calcined CZ(cp) and CZM(cp) catalyst.

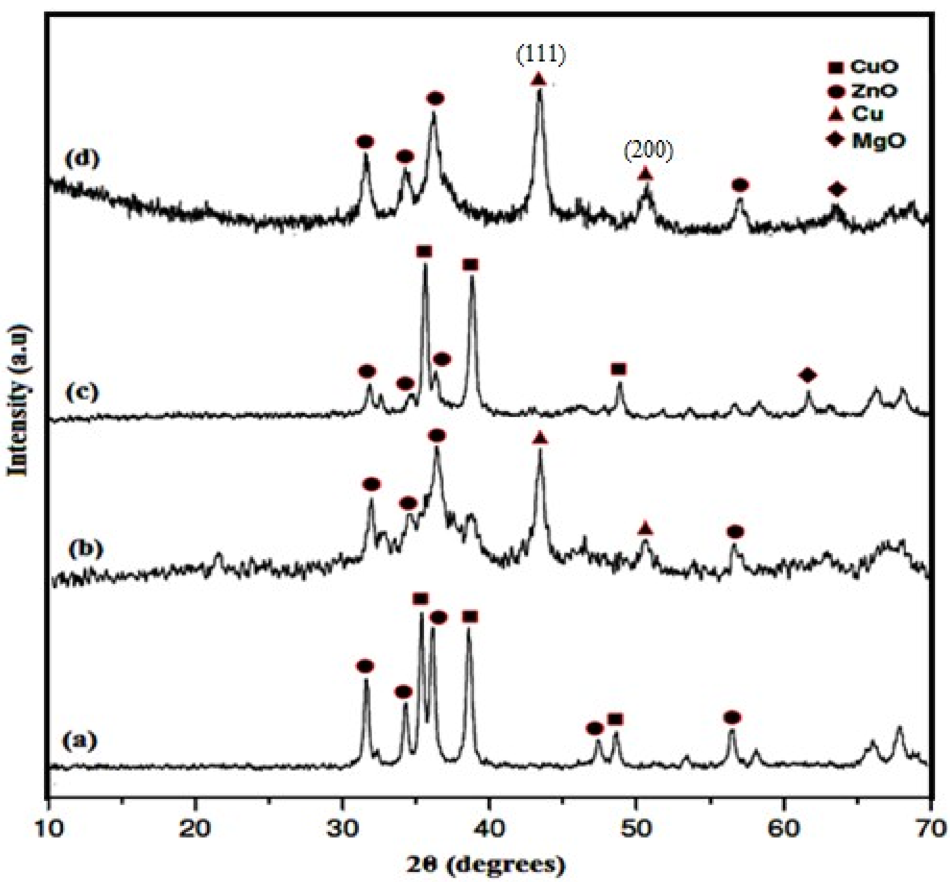


Figure: S3 XRD pattern of catalysts: (a) calcined CZ(F) (b) spent CZ (F) (c) calcined CZM(F) and (d) spent CZM(F).

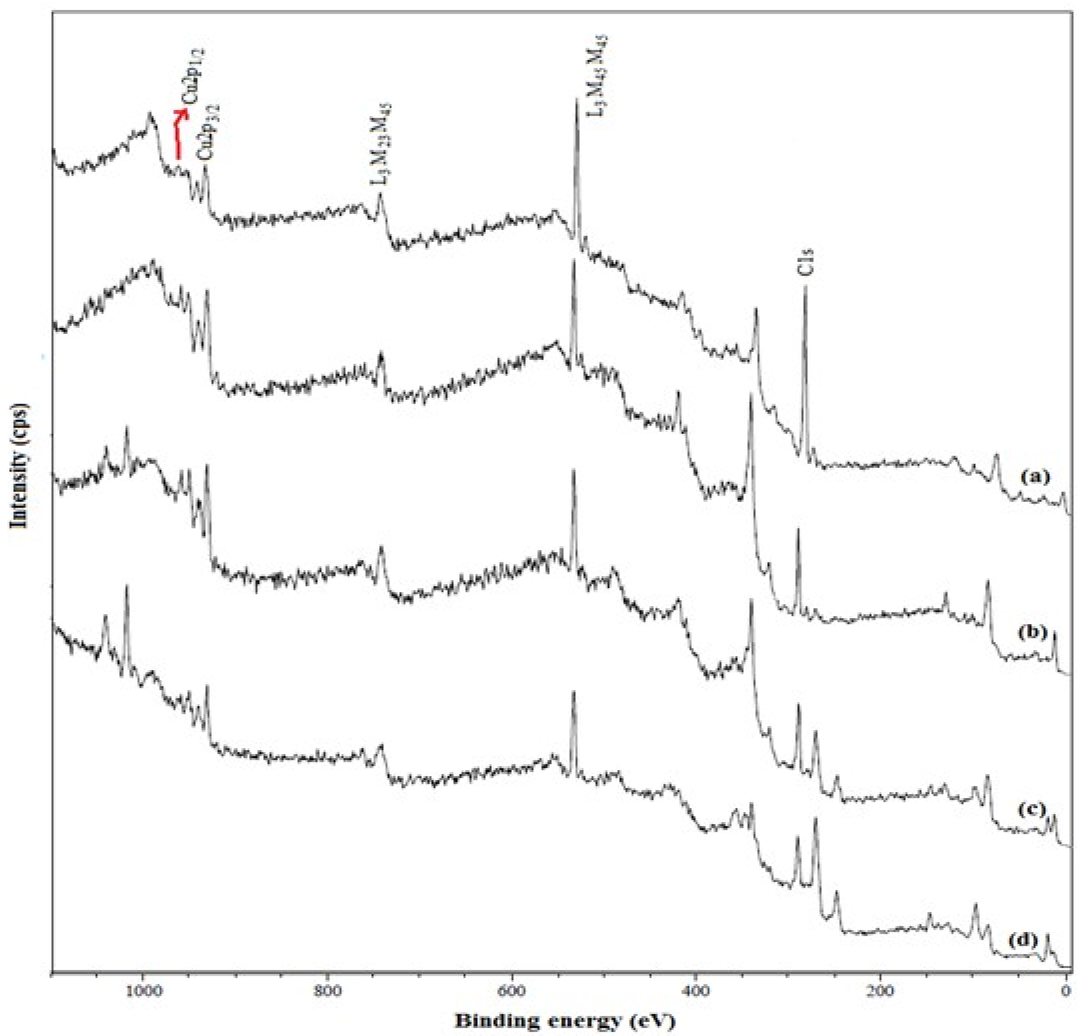
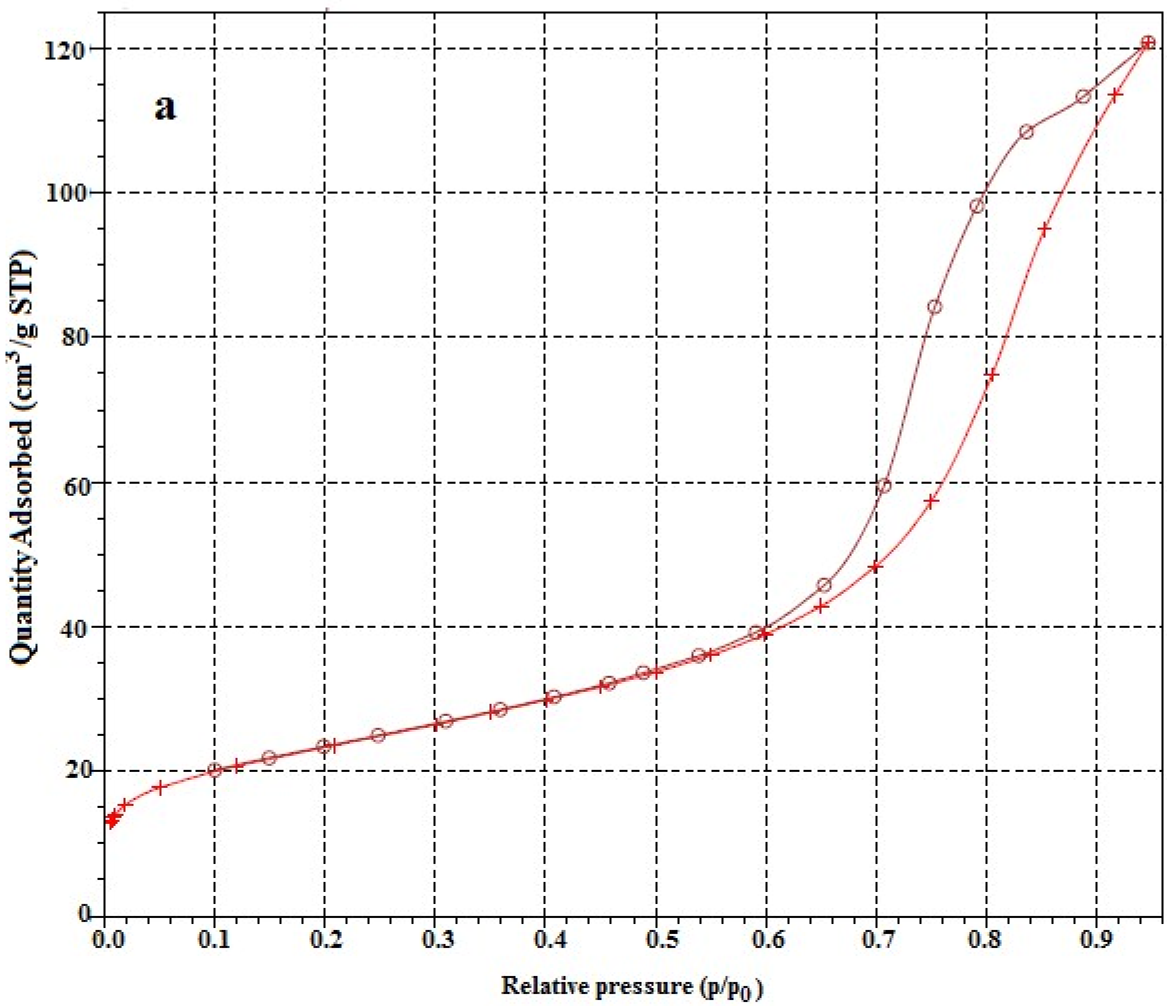
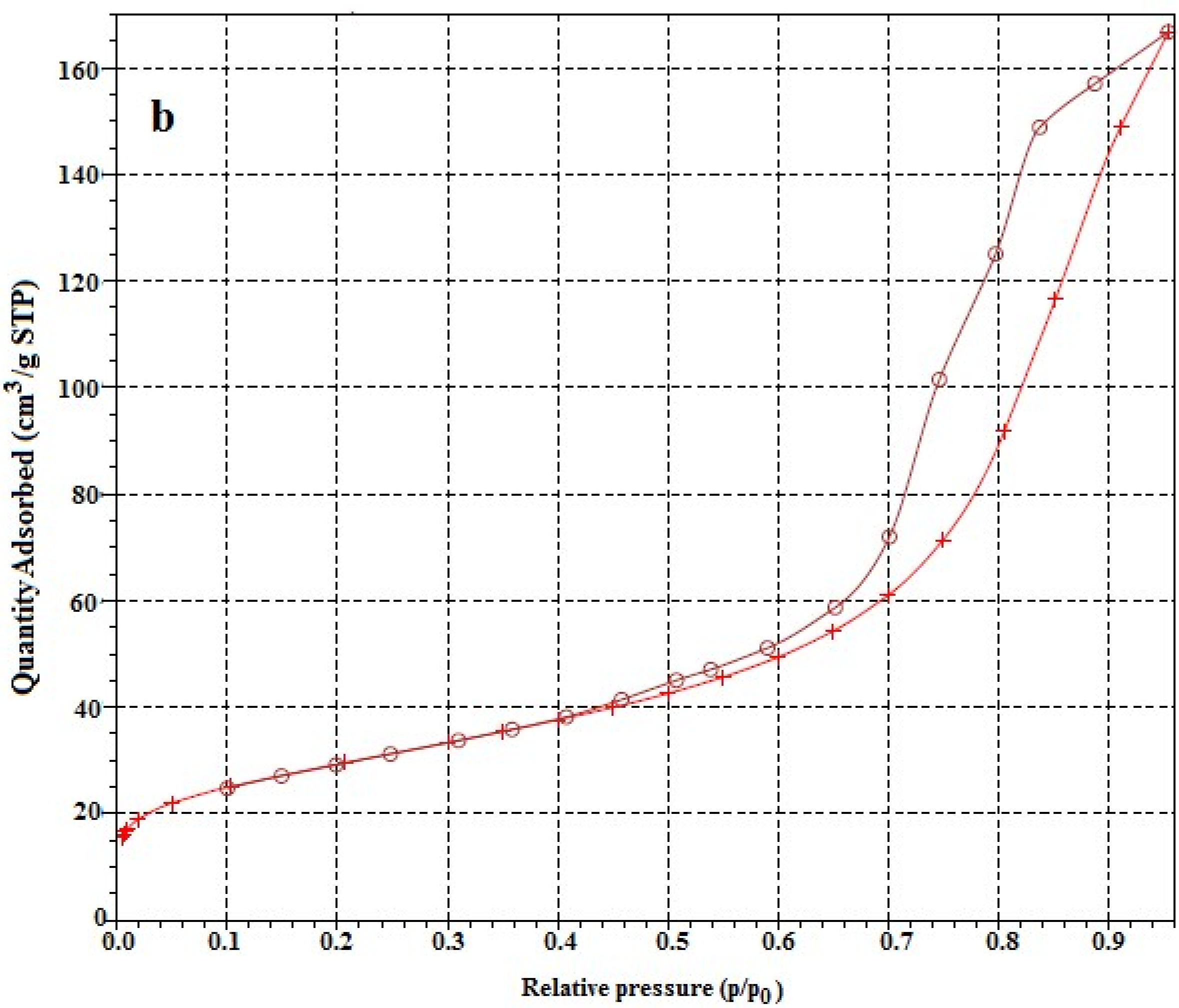
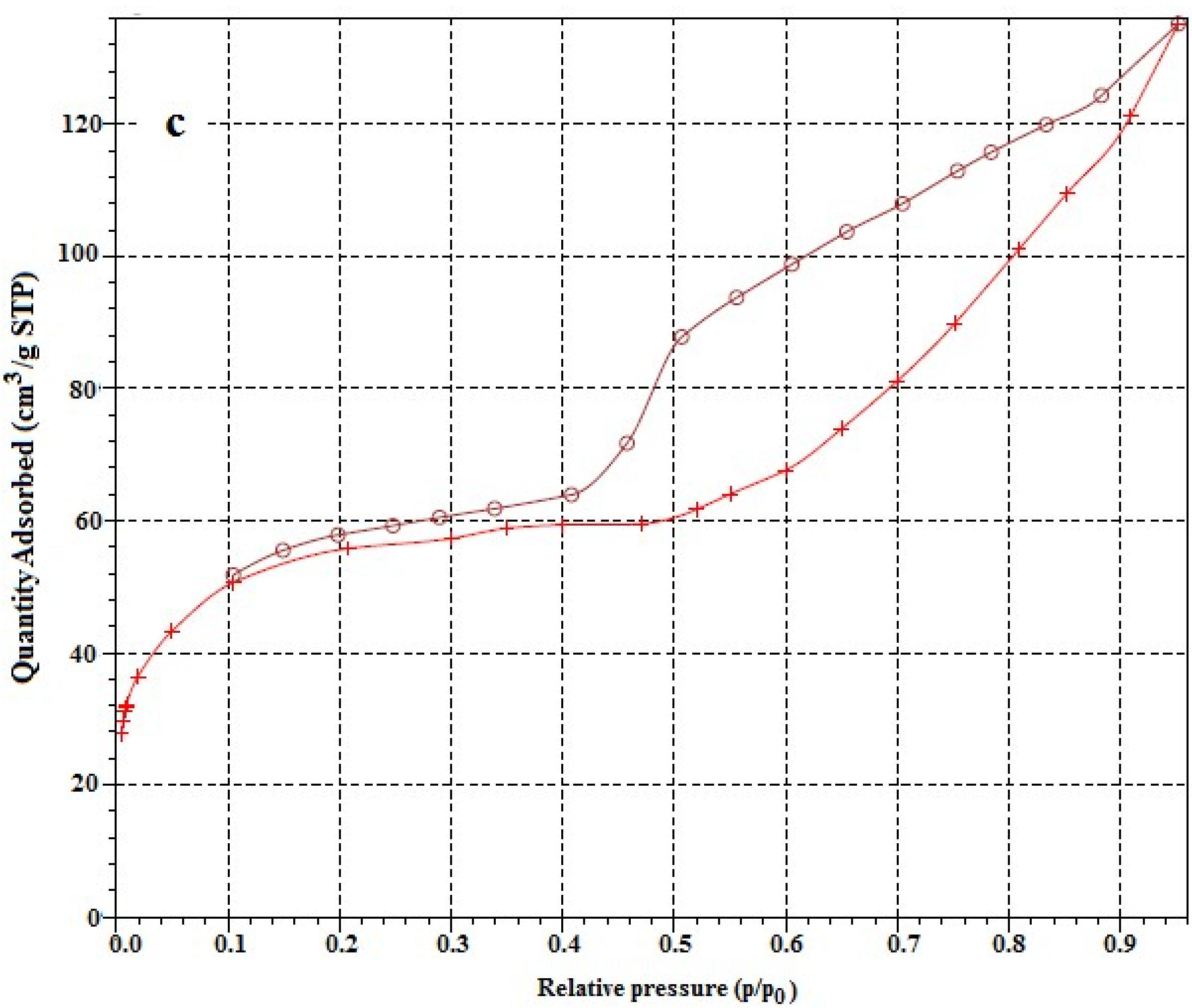


Figure: S4 Representative XPS survey spectra of (a) As synthesized Cu_2O (b) Standard Cu_2O (c) CZ(F) and (d) CZ(cp)


a
Quantity Adsorbed (cm^3/g STP)
Relative pressure (p/p$_0$)
0
20
40
60
80
100
120
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9



b
Quantity Adsorbed (cm3/g STP)
0
20
40
60
80
100
120
140
160
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Relative pressure (p/p0)



c
Quantity Adsorbed (cm3/g STP)
0
20
40
60
80
100
120
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Relative pressure (p/p0)

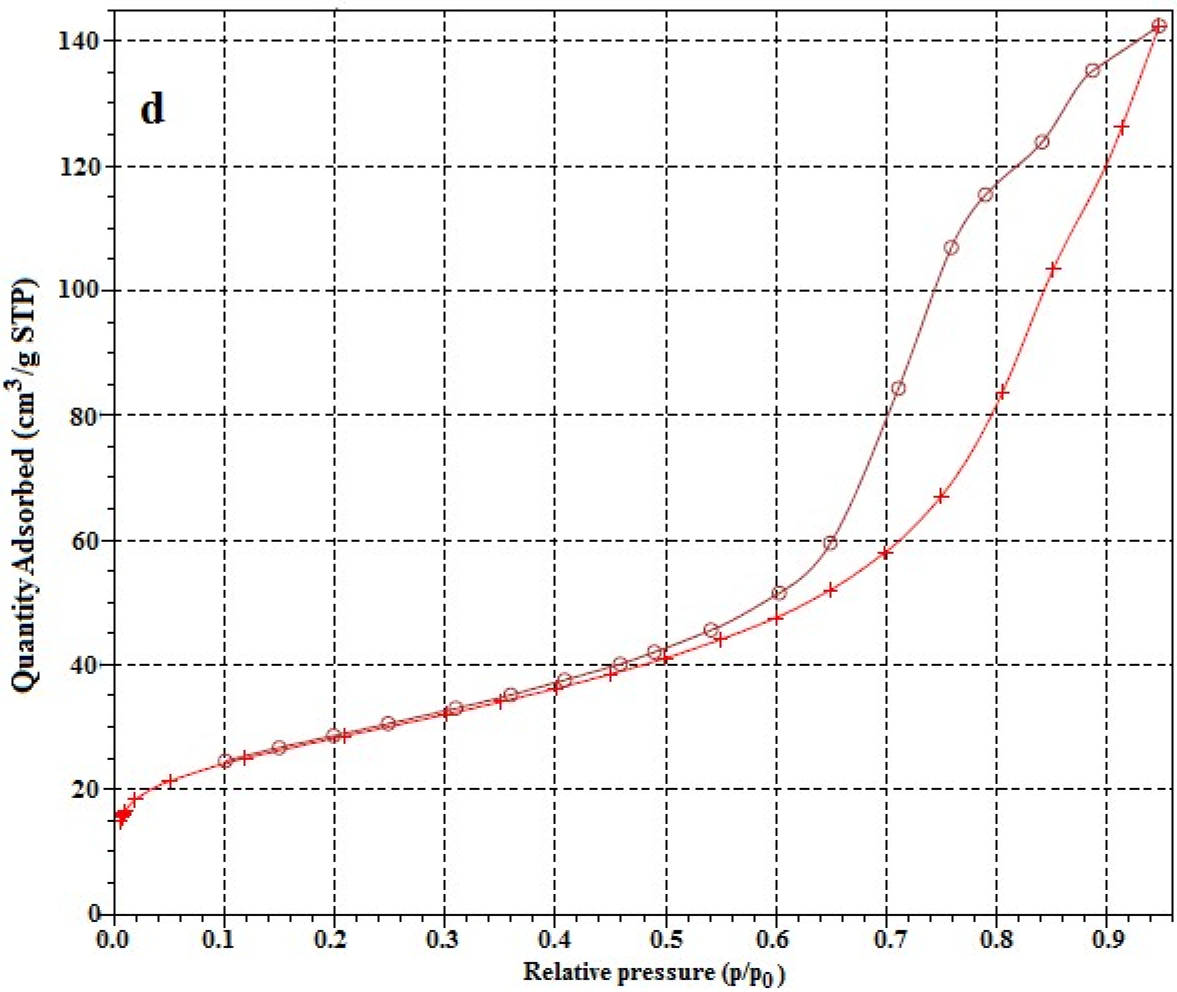


Figure: S5 N_2 adsorption isotherms of calcined hybrid catalysts (a) CZ (F); (b) CZ (cp); (c) CZM(F); (d) CZM(cp)

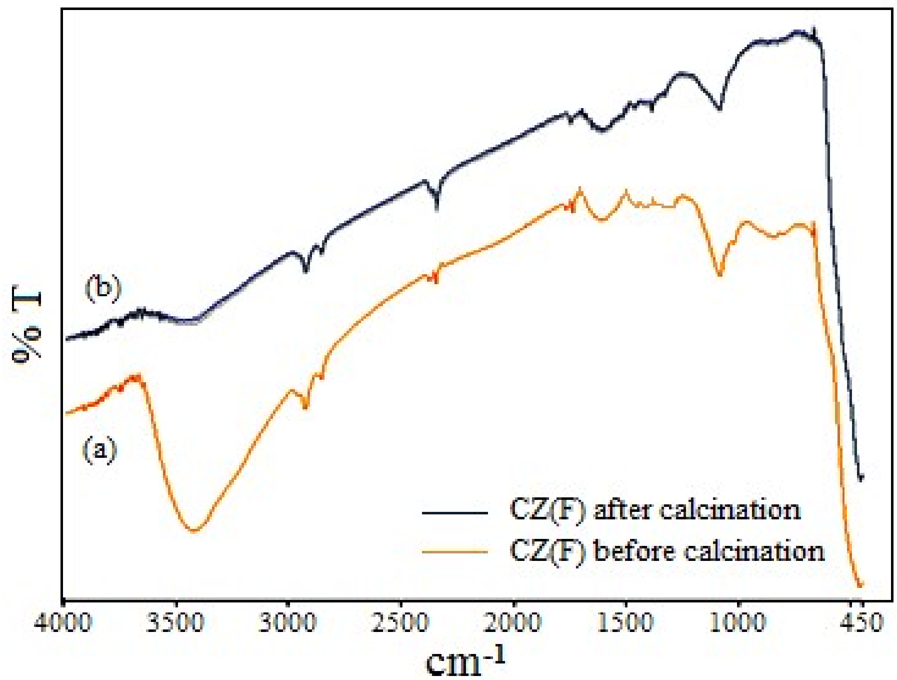


Figure: S6 IR analysis for CZ(F) (a) before calcination and (b) after calcination

Annexure 1: H_2/Cu ratio calculations

For CZM (F) catalyst

1 mol $Cu(NO_3)_2 \rightarrow$ ½ mol Cu_2O
0.55ᵠ mol $Cu(NO_3)_2 \rightarrow$ ½×0.55 mol Cu_2O
$\rightarrow$0.275 mol Cu_2O
$\rightarrow$0.275 mol × 143.09 g/mol
$\rightarrow \boxed{39.35g\ Cu_2O}$

1 mol $Zn(NO_3)_2 \rightarrow$ 1 mol ZnO
0.25ᵠ mol $Zn(NO_3)_2 \rightarrow$ 1 mol ZnO
$\rightarrow$0.25 mol × 81.408 g/mol
$\rightarrow \boxed{20.35g\ ZnO}$

1 mol $Mg(NO_3)_2 \rightarrow$ 1 mol MgO
0.20ᵠ mol $Mg(NO_3)_2 \rightarrow$ 1 mol MgO
$\rightarrow$0.20 mol × 40.305 g/mol
$\rightarrow \boxed{8.06g\ MgO}$

Total oxides: 39.35g Cu_2O + 20.35g ZnO + 8.06g MgO = **67.76g**

Amount of each component contained in 1g catalyst:
Cu_2O $\rightarrow$ (39.35) ÷ (67.76) **= 0.58g (0.004 mol)**
ZnO $\rightarrow$ (20.35) ÷ (67.76) **= 0.30g (0.0037 mol)**
MgO $\rightarrow$ (8.06) ÷ (67.76) **= 0.12g (0.0029 mol)**

Theoretically, according to the following equation:

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

1 mol Cu_2O will consume $\rightarrow$ 1 mol H_2
$\rightarrow$ 1000 mmol H_2
143.09 g Cu_2O will consume $\rightarrow$ 1000 mmol H_2
0.58 g Cu_2O will consume $\rightarrow \frac{1000\times0.58}{143.09}$ mmol H_2
$\rightarrow \boxed{\mathbf{0.4058 \times 10\ mmol\ H_2/g_{catalyst}}}$

Since other oxides viz. ZnO and MgO are non reducible oxides in the temperature range of TPR analysis, the H_2 consumption will be only for Cu_2O.

Since 1 g catalyst contains 0.004 Cu_2O moles
1 mol Cu_2O will give $\rightarrow$ 2 mol Cu
0.004 mol Cu_2O will give $\rightarrow$ 2×0.004 mol Cu
$\rightarrow$ 0.008 mol Cu
$\rightarrow$ 0.8 ×10 mmol Cu

We observed that as per TPR experiment, consumption of H_2 per gram of catalyst = **0.41×10 mmol/g_{cat}**

Thus, $\boxed{\mathbf{H_2/Cu\ ratio = 4.1/8 = 0.51}}$

For CZM (cp) catalyst

1 mol $Cu(NO_3)_2 \rightarrow$ 1 mol CuO
0.55ᵠ mol $Cu(NO_3)_2 \rightarrow$ 0.55 mol CuO
$\rightarrow$0.55 mol × 79.545 g/mol
$\rightarrow \boxed{43.75\ CuO}$

1 mol $Zn(NO_3)_2 \rightarrow$ 1 mol ZnO
0.25ᵠ mol $Zn(NO_3)_2 \rightarrow$ 1 mol ZnO
$\rightarrow$0.25 mol × 81.408 g/mol
$\rightarrow \boxed{20.35g\ ZnO}$

1 mol $Mg(NO_3)_2 \rightarrow$ 1 mol MgO
0.20ᵠ mol $Mg(NO_3)_2 \rightarrow$ 1 mol MgO
$\rightarrow$0.20 mol × 40.305 g/mol
$\rightarrow \boxed{8.06g\ MgO}$

Total oxides: 43.75g Cu_2O + 20.35g ZnO + 8.06g MgO **= 72.16g**

Amount of each component contained in 1g catalyst:
Cu_2O $\rightarrow$ (43.75) ÷ (72.16) **= 0.61g (0.0076 mol)**
ZnO $\rightarrow$ (20.35) ÷ (72.16) **= 0.28g (0.0034 mol)**
MgO $\rightarrow$ (8.06) ÷ (72.16) **= 0.11g (0.0027 mol)**

Theoretically, according to the following equation:

$$CuO + H_2 \rightarrow Cu + H_2O$$

1 mol CuO will consume $\rightarrow$ 1 mol H_2
$\rightarrow$ 1000 mmol H_2
79.545 g CuO will consume $\rightarrow$ 1000 mmol H_2
0.61 g CuO will consume $\rightarrow \frac{1000\times0.61}{79.545}$ mmol H_2
$\rightarrow \boxed{\mathbf{0.7669\times10\ \ mmol\ H_2/g_{catalyst}}}$

Since other oxides viz. ZnO and MgO are non reducible oxides in the temperature range of TPR analysis, the H_2 consumption will be only for CuO.

Since 1 g catalyst contains 0.007 CuO moles
1 mol CuO will give $\rightarrow$ 1 mol Cu
0.0076 mol CuO will give $\rightarrow$ 0.0076 mol Cu
$\rightarrow$ 0.76×10 mmol Cu

We observed that as per TPR experiment, consumption of H_2 per gram of catalyst = **0.7828×10 mmol/g_{cat}**

Thus, $\boxed{\mathbf{H_2/Cu\ ratio = 7.828/7.6 = 1.0}}$

This is close to the ratio obtained by theoretical calculations.

(ᵠ moles taken to prepare catalyst)