Supplementary data

2. Experimental

- **Characterization of Pristine MWCNT and MC**

Multiwalled carbon nanotubes (MWCNT) was purchased from Reinste Nano ventures Pvt. Ltd and Mesoporos carbon (MC) from Sigma Aldrich, their characteristics are given below (Fig. S1, S2 and S3).

a) Powder X-ray diffraction (Powder XRD)

The diffraction peaks at 25.9° and 43.9° corresponds to (002), (100) hkl planes of the graphite structure of MWCNT shown in Fig. S1(a). The diffraction peaks for MC observed at 28.8° and 43.4° corresponds to (002) and (100) diffraction planes of hexagonal graphitic carbon (Fig. S1b).

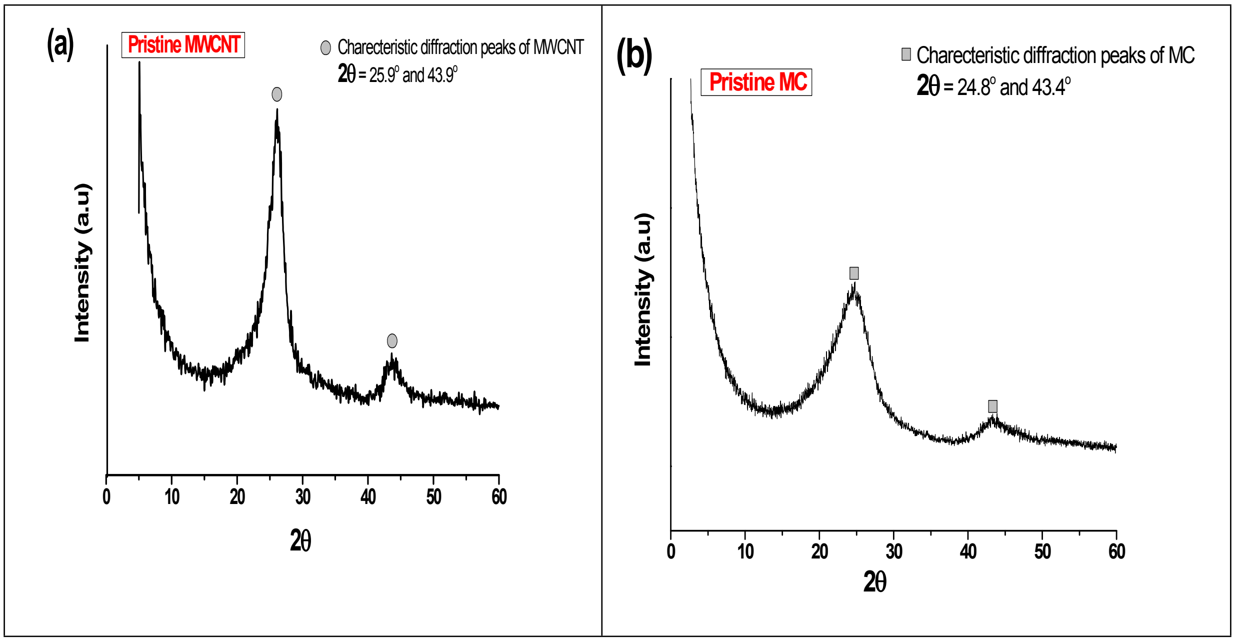
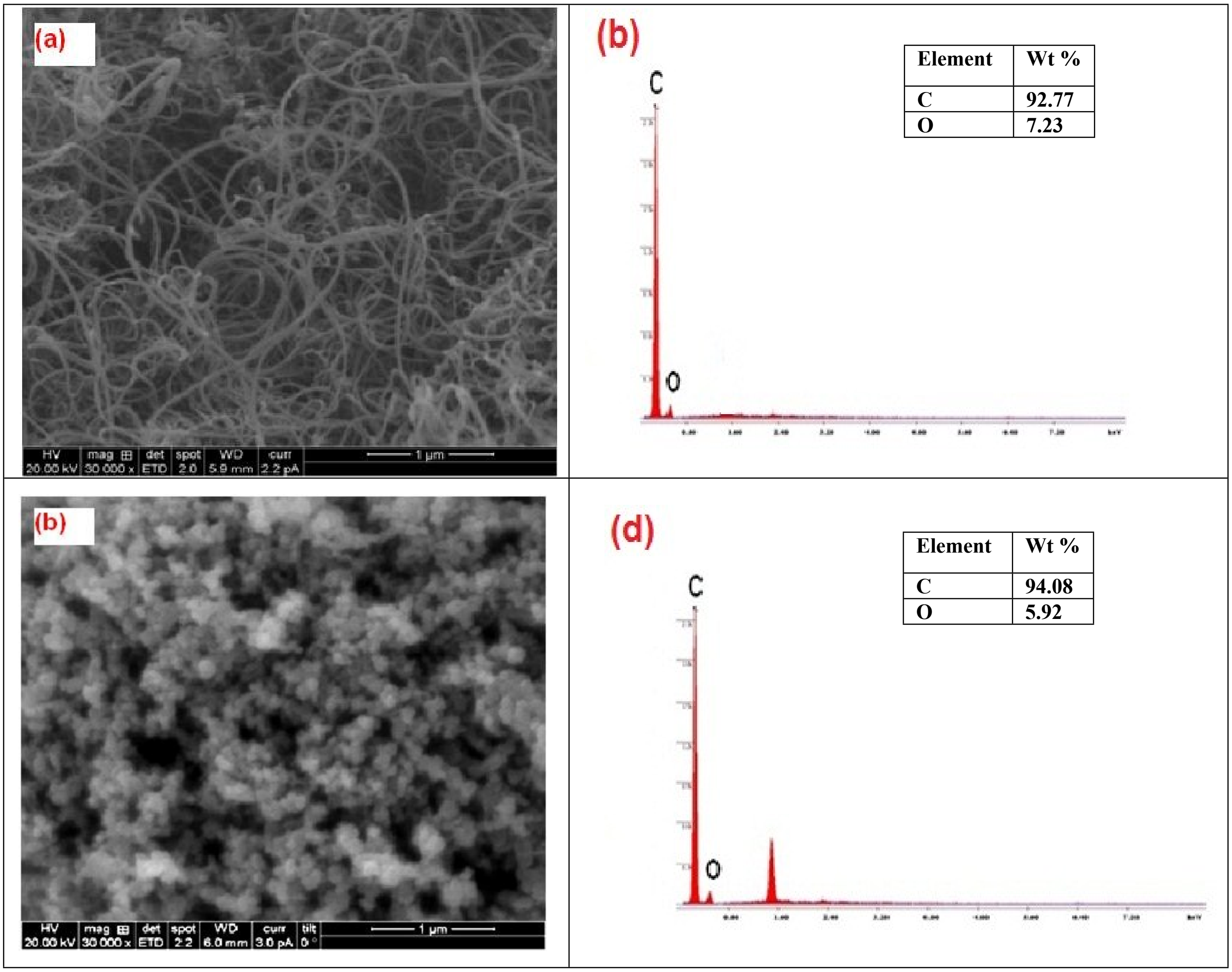


Fig. S1. Powder XRD Pattern of a) pristine MWCNT and b) pristine MC.

b) SEM-EDS

SEM images and EDS profiles of pristine MWCNT and pristine MC are shown in Fig. S2. SEM images indicate the presence of tubular structures in MWCNT and in case of MC material porous structures are observed. The EDS profile of the pristine MWCNT and MC materials included along with the SEM images gives the atomic percentages of carbon and oxygen.



Element	Wt %
C	92.77
O	7.23

Element	Wt %
C	94.08
O	5.92

Fig. S2. SEM image and EDS profile of pristine MWCNT (a, b) and pristine MC (c, d).

c) TEM Analysis

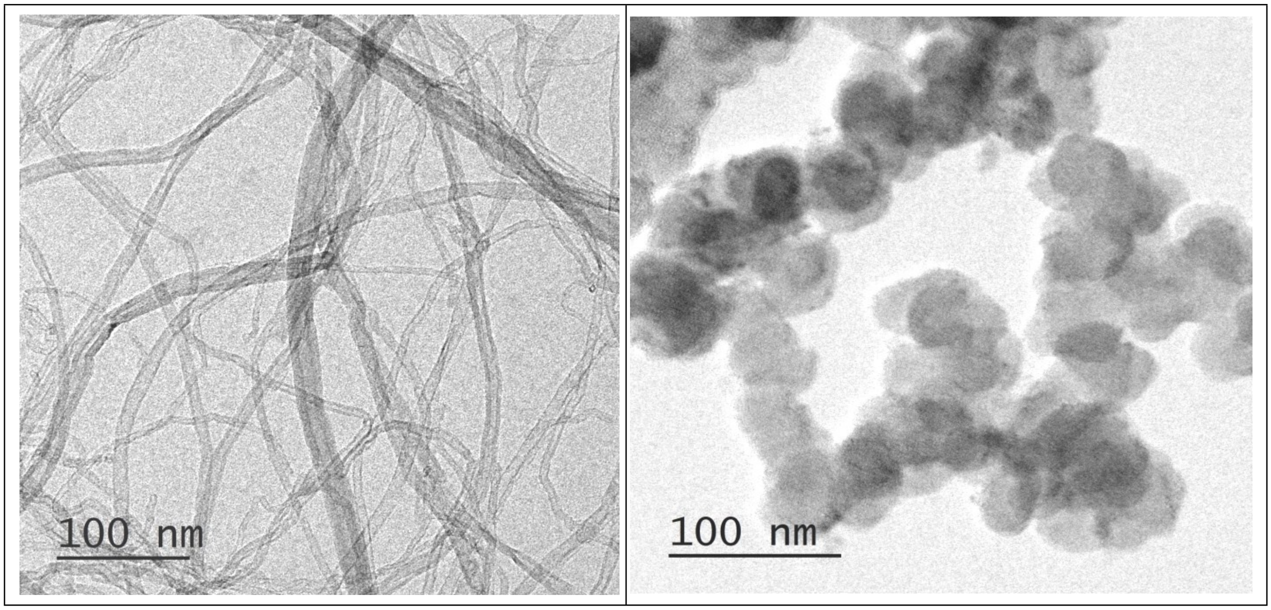


Fig. S3. TEM image of (a) pristine MWCNT and (b) pristine MC.

2.1. Preparation of MWCNT and MC supported single and bimetal catalysts

- **Acid activation of MWCNT and MC**

It is well reported in the literature that activation of carbon materials (MWCNT and MC) by acid treatment generates chelating groups for instance –COOH, –OH etc. The oxygen functionalities thus developed on the surface of the support interact with metal salts, which promote high dispersion of metal/s particles *via* impregnation with aqueous solution of metal salts. Finally, leading to high dispersion of metal/s particles stabilized within the pores of the support.

In a typical procedure, 0.5 g of MWCNT and MC were separately treated with a mixture of Conc. HNO_3 and Conc. H_2SO_4 (1:3) in a round bottom flask and heated on a mantle at 80 ^oC for 6 h. The contents of the flask were cooled to room temperature and mixed thoroughly with 2 L of deionized water using a magnetic stirrer. The solid was separated by filtration and washed with deionized water until the filtrate was neutral to pH test. These acid activated MWCNT and MC were dried in an air oven at 110 ^oC overnight. The materials thus obtained were abbreviated as F/MWCNT (Functionalized multiwalled carbon nanotubes) and F/MC (Functionalized mesoporous carbon) and stored in a desiccator.

- **Preparation of metal/s supported carbon materials**

Metal/s supported on F/MWCNT and F/MC were prepared by in situ reduction of metal/s halides in an aqueous solution. Monometallic catalysts with 10 % Cu or 1 % X (where X = Fe, Co, Ni, Zn and Ru) supported on MWCNT and MC were prepared by the following procedure. 0.5 g of F/MWCNT or F/MC was placed in 200 mL of deionized water and ultrasonicated for 30 min to obtain uniform dispersion of the carbon material in water. To this suspension 25 mL of a solution containing calculated amount of $CuCl_2.2H_2O$ or other transition metal halide was added followed by a drop wise addition of 100 mL of 0.2 % aqueous solution of $NaBH_4$. After complete addition, the reaction mixture was stirred at room temperature for 24 h. The solid in the resultant mixture was separated by filtration and washed several times with deionized water and two times with 5 mL portions of ethanol. The solid thus obtained was dried at 110 ^oC for 12 h and stored in a desiccator until further use. Similarly, bimetallic catalysts with 10 % Cu and 1 % X (where, X = Fe, Co, Ni, Zn and Ru) supported on MWCNT and MC were prepared by taking an appropriate mixture of two salt solutions and adopting the same procedure as given under the preparation of monometallic catalyst.

Characterization of the catalysts

In order to understand the relationship between catalytic activity and physicochemical properties the materials, a few selected catalysts such as F/MWCNT, F/MC, Cu-Ru/MWCNT, Cu-Ni/MWCNT, Cu-Ru/MC and Cu-Ni/MC were characterized the following techniques.

Powder XRD patterns were recorded on a Panalytical Xpert pro X-ray diffractometer using Cu Kα radiation (λ= 0.154 nm) in the 2θ range of 2^o–80^o with a scanning rate of 2^o min^{-1}. X-ray photoelectron spectra were performed using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Al Kα radiation (300 W, 15 kV and 1486.6 eV) with a multi-channel detector. Binding energies were reported as measured without correction. The catalyst particle morphology and elemental composition were investigated by SEM–EDS (Quanta 200 FEI). TEM images were obtained on Tecnai transmission electron microscope. N_2 adsorption-desorption isotherms were measured on a Quantachrome Autosorb-6b static volumetric instrument. The samples were de-gassed at 150 ^oC for 1 h prior to the measurements. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method and the average pore diameter and pore size distributions by the Barret–Joyner–Halenda (BJH) method using the desorption branch.

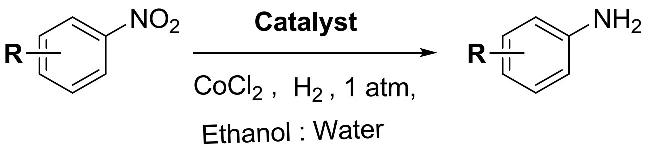
3. Results and Discussion

3.1. Catalytic activity studies

Initially the catalytic activity of the prepared materials was investigated in the hydrogenation of α, β-unsaturated aldehydes (Ex. Cinnamaldehyde and Crotonaldehyde) and the reduction of 4-bromo nitrobenzene.

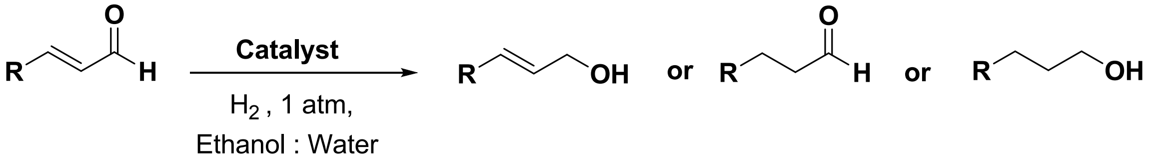
Catalytic activity tests were carried out in a 100 mL three necked flask fitted with water cooled reflux condenser. 0.1 g of the catalyst was added to the flask and heated at 100 ºC in a silicon oil bath for 30 min. Then, hydrogen gas was passed at the rate of 30 mL/min for 1 h. This was followed by the addition of 1 mmol of the organic substrate dissolved in 20 mL of 9:1 ethanol and water mixture through another neck of the flask using a syringe. In the case of reduction of nitroarenes, 0.5 mmol of anhydrous $CoCl_2$ was also added along with the substrate (Scheme 1 & 2). The progress of the reaction was monitored by TLC analysis of the reaction mixture samples withdrawn at different intervals. The reaction products were analyzed by gas chromatography (Shimadzu GC, model- GC2014AF) equipped with a flame ionization detector and stainless steel packed column (2 m) with 10 % RTX stabilwax silcoport.

After completion of the reaction, the contents of the flask were cooled to room temperature and filtered to recover the solid catalyst. The solvent was removed in a rotavap and the residue was purified by silica gel column chromatography using a mixture of n–hexane and ethyl acetate ratio (7:3) as eluent. The products were further analyzed by M.P, FT–IR, ^{1}HNMR and LC–MS analytical methods. Infrared spectra were recorded by KBr pellet method using Nicolet Model Impact 400D FT–IR spectrometer with 4 cm^{-1} resolution. ^{1}HNMR spectra were obtained using DMSO-d_6 as the solvent at 400 MHz using Bruker Advance NMR spectrometer. The spectra were referenced to TMS ($\delta = 0$ ppm) and melting point of the products was recorded in open capillary tube and are uncorrected. The mass spectral analysis was done on LC–MS Shimadzu QP 5000 instrument.



R= 4-NH_2, 4-Br, 4-F, 4-Cl, 4-CN etc.

Scheme 1. Hydrogenation of nitroarenes in the presence of Cu/X/ MWCNT or Cu/X/MC as catalysts (X= Fe, Co, Ni, Zn and Ru).



R= C_6H_5 (Cinnamaldehyde) or CH_3 (Crotanaldehyde).

Scheme 2. Hydrogenation of α, β- unsaturated aldehydes in the presence of Cu/X/ MWCNT or Cu/X/MC as catalysts (X= Fe, Co, Ni, Zn and Ru).

Optimization of hydrogenation of cinnamaldehyde using molecular hydrogen as hydrogen source in presence of Cu-Ru/MWCNT catalyst.

Catalytic activity of Cu-Ru/MWCNT was further investigated using molecular hydrogen, to study the effect of varying the solvent, temperature and duration of the reaction, amount of the catalyst and optimize the reaction conditions to get the best yield and selectivity of the alcohol product in the hydrogenation of cinnamaldehyde. The results are presented below.

Effect of solvent

The effect of solvents such as methanol, ethanol, isopropyl alcohol, THF, DMF, chloroform, DCM and 9:1 mixture of ethanol and water were investigated on the selectivity of cinnamyl alcohol in the hydrogenation of cinnamaldehyde and the results are given as supplementary data in Fig. S4. The selectivity towards cinnamyl alcohol was found to be good with polar solvents like methanol, ethanol and isopropanol and ethanol:water mixture. In the presence of methanol, ethanol and isopropyl solvent some amount of diacetal formation was detected. A mixture of 9:1 ethanol and water was found to be the best solvent medium in which the % selectivity of cinnamyl alcohol was 78 % and there is was diacetal formation. Increasing in polarity of the alcohol solvent there is slight increase in the cinnamyl alcohol selectivity. These observed results could be due to the hydrogen bonding between carbonyl oxygen and hydroxyl group of the alcohols and also it may be due to higher solubility of H_2 in polar solvents.[22, 42] In presence of DMF conversion of the substrate was low; it might be due to the poor solubility of the reactant in it.

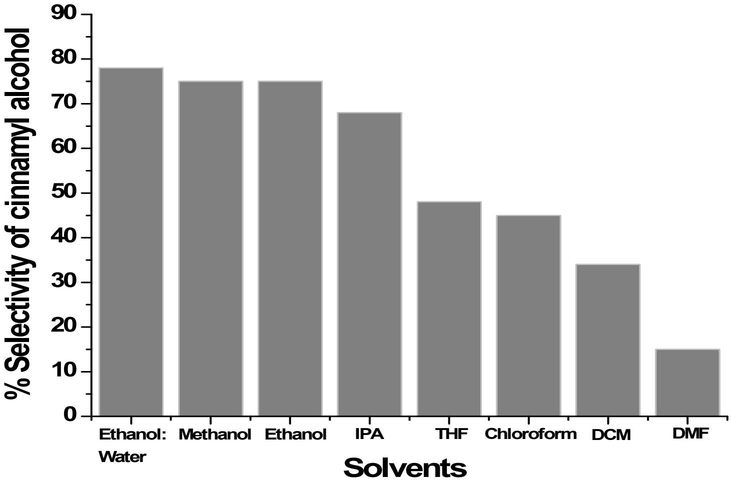


Fig. S4. Effect of solvents on % selectivity of cinnamyl alcohol, *Reaction conditions:* 1 mmol of cinnamaldehyde, 0.1 g of catalyst at 100 °C for 1 h.

Effect of temperature and duration of the reaction

Initially when hydrogenation of cinnamaldehyde (**I**) was conducted at room temperature there was no progress in the reaction even after 2 h. The temperature of the reaction mixture was raised from 40 to 140 °C with an interval of 20 °C. Each of these reactions was carried out for different durations such as 15, 30, 45, 60, 120 and 180 min. The results with respect to the % yield of the unsaturated alcohol are given in supplementary data (Fig. S5).

Maximum selectivity for cinnamyl alcohol (**II**) was observed in a reaction conducted at 80 °C for 60 min. At this temperature the selectivity remained constant even for a reaction conducted up to 120 min. However, beyond this time selectivity for **II** reduced and that of hydrocinnamyl alcohol (**VI**) increased. Further above 80 °C there was a significant decrease in the selectivity of **II** and increased that of **VI.** These studies thus confirmed a reaction temperature above 80 °C is not suitable for the cinnamyl alcohol production.

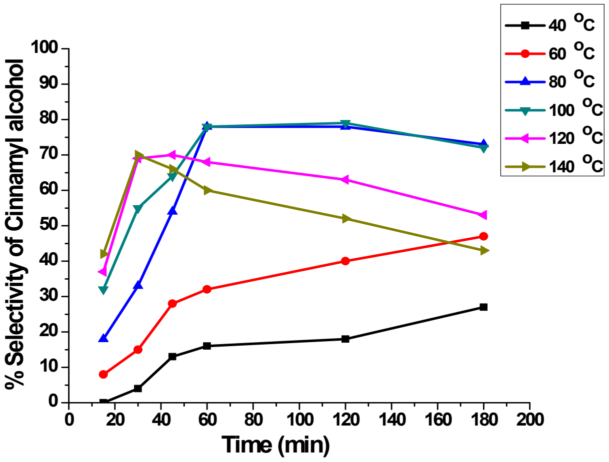


Fig. S5. Effect of reaction time and temperature on % selectivity of cinnamyl alcohol. *Reaction conditions:* 1 mmol of cinnamadehyde, 0.1 g of catalyst and ethanol: water (9:1) as solvent.

Effect of the amount of catalyst

The catalytic activity of the catalyst was measured in the hydrogenation of **I** by varying the amount of the catalyst from 0.01 g to 0.2 g. The catalytic activity increased with increasing catalyst amount and there was no improvement in percentage yield of the product above 0.08 g. Thus, 0.08 g seems to be optimum amount of catalyst required for the reaction (Fig. S6). It was noticed that above 0.1 g of the catalyst the selectivity for **II** decreases and formation of **VI** increases.

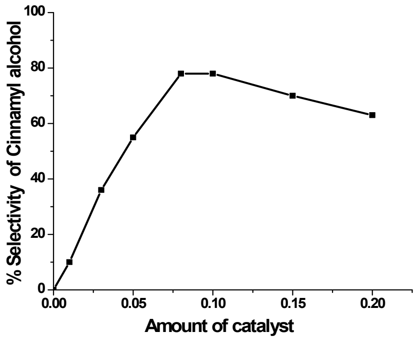


Fig. S6. Effect of catalyst amount on % selectivity of cinnamyl alcohol. (a*) Reaction conditions:* 1 mmol of cinnamaldehyde, 80 ^{o}C for 1 h and ethanol: water (9:1) as solvent.

Recyclability of Cu-Ru/MWCNT and Cu-Ru/MC catalysts in the hydrogenation of cinnamaldehyde

Cu-Ru/MWCNT and Cu-Ru/MC catalysts were checked for their reusability in the hydrogenation of **I** in 9:1 ethanol and water mixture as solvent. After completion of the reaction the catalyst was separated from the reaction mixture and washed with deionized water followed by acetone. The catalyst was dried at 120 °C in a hot air oven for 12 h and reused in a fresh reaction.

Cu-Ru/MWCNT catalyst was found to be recyclable up to 5 times without any alteration in its, selectivity for **II**. However, Cu-Ru/MC catalyst exhibited decreased % selectivity for **II** with an increase in number of cycles as shown in Fig. S7(a). Further separation of the catalyst from the reaction mixture was more difficult in the case of Cu-Ru/MC catalyst than Cu-Ru/MWCNT catalyst. Here it is worth mentioning that, analysis of the recycled catalysts made by ICP-OES method to estimate Cu and Ru contents indicated that there was no significant leaching of Cu and Ru nanoparticles from the surface of MWCNT. Whereas, MC based catalysts showed increased leaching of Cu and Ru particles with increase in number of recycles (Fig. S7(b)). The recyclability of the catalysts demonstrates Cu and Ru species are the catalytic active sites dispersed over carbon a support that plays a synergetic role in this reaction.

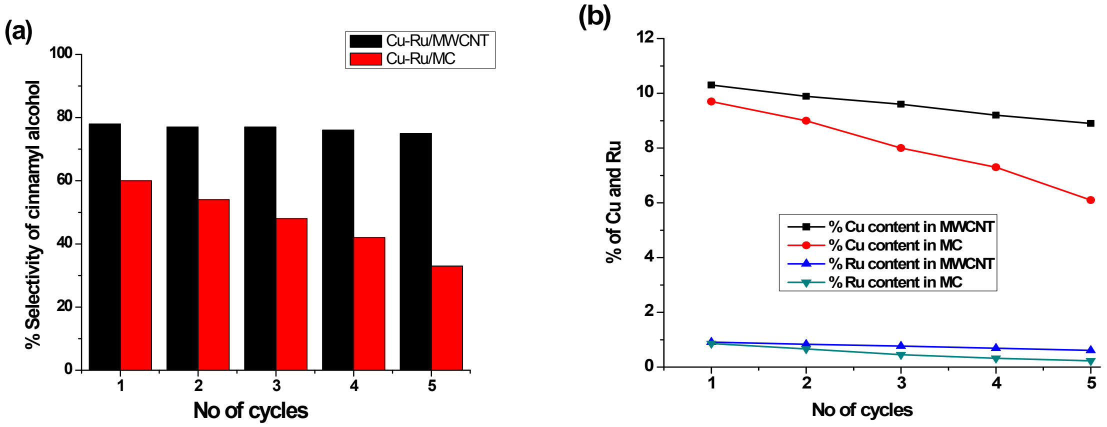


Fig. S7. Recyclability test of Cu-Ru/MWCNT and Cu-Ru/MC catalysts, **(a)** % selectivity of cinnamyl alcohol **(b)** ICP–OES results on Cu and Ru contents, Reaction conditions: 1 mmol of cinnamaldehyde, 0.08 g of catalyst, 80 °C, 1 h and ethanol: water (9:1) as solvent.

Mechanism for the reduction of 4-bromo nitrobenzene to 4-bromo aniline

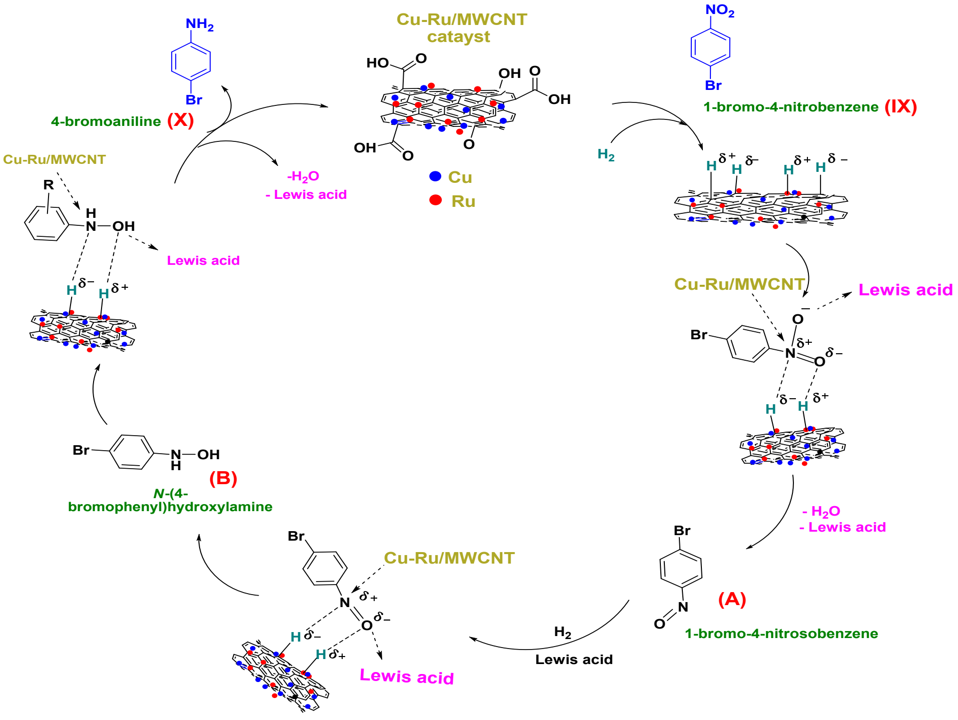


Fig. S8. A plausible reaction mechanism for the reduction of 4-bromo nitrobenzene to 4-bromo aniline using Cu-Ru/MWCNT catalyst with molecular H_2 and Lewis acid.

Optimization of the 4-bromo nitrobenzene reduction reaction using $NaBH_4$ as hydrogen source in presence of Cu-Ru/MWCNT catalyst

Catalytic activity of Cu-Ru/MWCNT was further investigated using $NaBH_4$ as hydrogen source in the reduction of 4-bromo nitrobenzene by varying solvent effect, temperature and duration of the reaction and amount of the catalyst. The results are presented below.

Effect of the solvent

The effect of solvents such as methanol, ethanol, isopropyl alcohol, THF, DMF, chloroform, DCM and ethanol: water (9:1) was investigated in the reduction of 4-bromo nitrobenzene to 4-bromo aniline using Cu-Ru/MWCNT catalyst (Fig. S9). It is noteworthy that, the % yield of 4-bromo aniline was found to be good with polar solvents like methanol, ethanol and isopropanol and ethanol: water mixture. The % selectivity and yield of the product was found to be best with ethanol: water mixture (9:1). This is due to high solubility of hydrogen gas in alcohols, these solvents accelerate $–NO_2$ reduction.[42] It is worth mentioning that no debromination was observed in these polar solvents. It is also interesting to note that in polar aprotic solvents like THF and DMF, N-(4-bromophenyl) hydroxylamine (**XII**) was the major product observed and yield of 4-bromoaniline is less than 15 %. In other solvents like chloroform and DCM, yield of the product was less (45–37 %), this might due to the less solubility of 4-bromo nitrobenzene in these solvents.

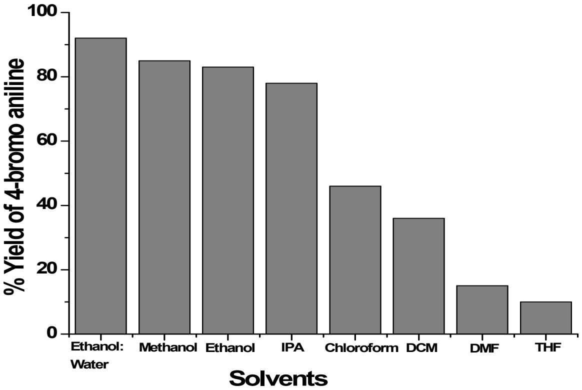


Fig. S9. Effect of solvents on % yield of 4-bromoaniline, *Reaction conditions*: 1 mmol of 4-bromo nitrobenzene, 0.1 g catalyst, RT for 30 min and ethanol: water (9:1) as solvent.

Effect of temperature and duration of the reaction

Reduction of 4-bromo nitrobenzene was also subjected to study the effect of temperature and duration of the reaction using 0.1 g of Cu-Ru/MWCNT. It was noticed that reaction favors at room temperature and affords high product yield, above 40 ^{o}C product yield and selectivity decreases due to the formation of debrominated product (**XI**) shown in supplementary data (Fig. S10).

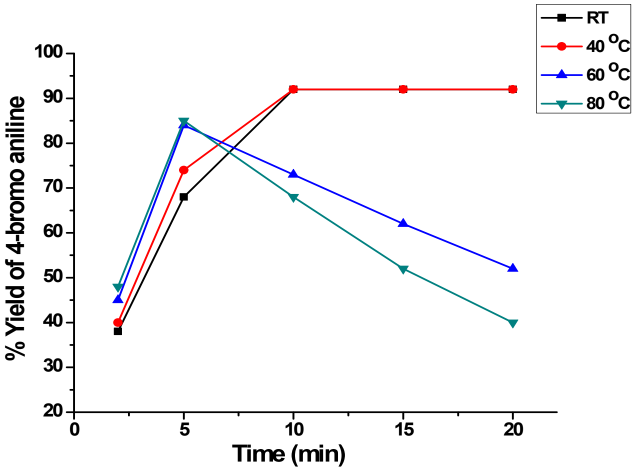


Fig. S10. Effect of reaction time and temperature on % yield of 4-bromoaniline, *Reaction conditions:* 1 mmol of 4-bromo nitrobenzene, 0.1 g of catalyst and ethanol: water (9:1) as solvent.

Effect of the amount of catalyst

Initially the catalytic activity of Cu-Ru/MWCNT was measured in the reduction of 4-bromo nitrobenzene by varying catalyst amount from 0.01 g to 0.2 g. The catalytic activity increased with increasing amount of the catalyst and there was no further improvement in % yield of the product above 0.1 g of the catalyst. Thus, 0.1 g seems to be the optimum amount of catalyst required for the reaction, results are shown in supplementary data (Fig. S11). It was observed that upon increasing the catalyst weight above 0.1 g, the selectivity of 4-bromoaniline decreased and that of the debrominated product increased.

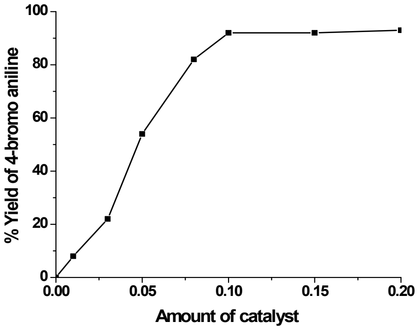


Fig. S11. Effect of catalyst amount on % yield of 4-bromoaniline, *Reaction conditions:* 1 mmol of 4-bromo nitrobenzene, RT for 10 min and ethanol: water as solvent (9:1).

Recyclability of Cu-Ru/MWCNT and Cu-Ru/MC catalysts in the reduction of 4-bromo nitrobenzene

As Cu-Ru/MWCNT and Cu-Ru/MC catalysts exhibited good catalytic activity in the reduction of 4-bromo nitrobenzene using $NaBH_4$ as hydrogen source, these two catalysts were further checked for their recyclability. Cu-Ru/MWCNT catalyst was found best recyclable catalyst (up to 5 times) maintaining the same % yield of the product, than Cu-Ru/MC. However, Cu-Ru/MC catalyst showed decreased in the % yield of the product with increase in number of cycles as shown in Fig. S12(a). Analysis of ICP-OES method indicates that no significant leaching of Cu and Ru nanoparticles on the surface of MWCNT was noticed. On the other hand mesoporous carbon based catalysts showed leaching of Cu and Ru particles gradually with increase in number of recycles (Fig. 12(b)). The recyclability of the catalysts confirms the synergetic role of Cu and Ru in the reduction of 4-bromo nitrobenzene.

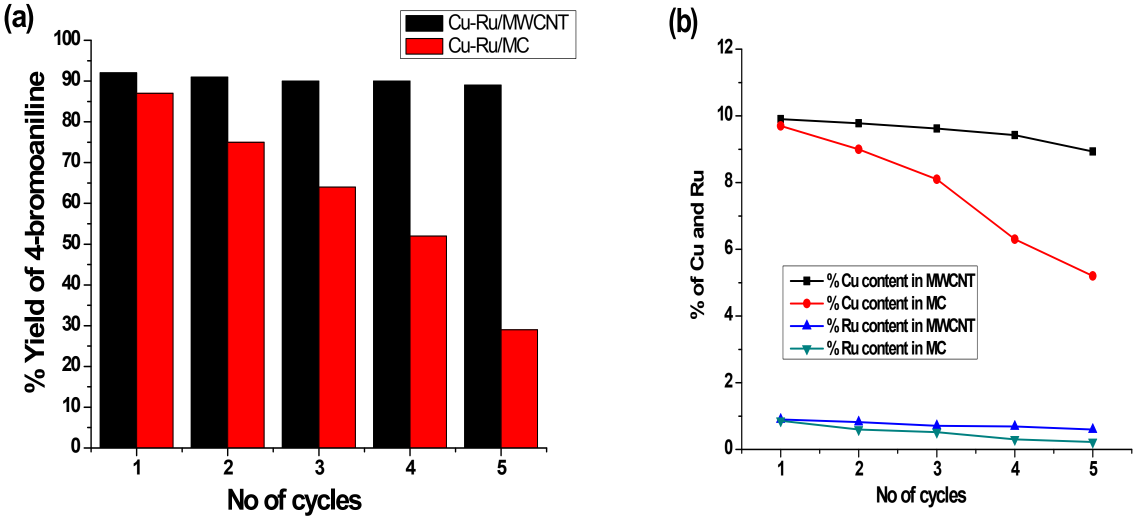


Fig. S12. Recyclability test of Cu-Ru/MWCNT and Cu-Ru/MC catalysts**.** **(a)** % yield of 4-bromoaniline, **(b)** ICP–OES results on Cu and Ru contents, Reaction conditions: 1 mmol of 4-bromo nitrobenzene, 0.1 g of catalyst, RT, 10 min and ethanol: water as solvent (9:1).

SD-1. Spectroscopic data some aromatic heterocyclic amino compounds

1. (4-aminophenyl)(pyrrolidin-1-yl)methanone (Table 7, Entry 1): White solid. M.P: 120–122 ^{o}C; IR (cm^{-1}): 3634, 3546, 3530, 1658, 1523, 1509, 1444, 1322, 1261; ^{1}HNMR (400 MHz, DMSO–d_6): δ 7.25 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 8.4$ Hz, 2H), 5.44 (s, 2H), 3.41–3.28 (m, 4H), 1.78–1.75 (m, 4H); MS (EI) m/z: 191.3 (M+1).

2. (4-aminophenyl)(piperidin-1-yl)methanone (Table 7, Entry 2): Pale yellow solid. M.P: 128–130 °C; IR (cm^{-1}): 3658, 3638, 3566, 3400, 2760, 1653, 1540, 1392, 1371, 899; ^{1}HNMR (400 MHz, DMSO–d$_6$): δ 7.3 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 2H), 3.41–3.28 (m, 6H), 1.78–1.75 (m, 4H); MS (EI) m/z: 206.1 (M+1).

3. (4-aminophenyl)(4-(5-methylpyrimidin-4-yl)piperazin-1-yl)methanone (Table 7, Entry 3): Yellow solid. M.P: 156–158 °C; IR (cm^{-1}): 3656, 3316, 2343, 1899, 1765, 1656, 1518, 1454, 1254, 1187; ^{1}HNMR (400 MHz, DMSO–d$_6$): δ 8.37 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.50 (s, 1H), 3.62–3.61 (m, 4H), 3.55–3.54 (m, 4H), 2.47 (s, 3H); MS (EI) m/z: 298.2 (M+1).

4. (4-aminophenyl)(4-(2-methoxypyridin-3-yl)piperazin-1-yl)methanone (Table 7, Entry 4): Yellow solid. M.P: 140–143 °C; IR (cm^{-1}): 3343, 3252, 2923, 1655, 1639, 1531, 1478, 1370, 1077, 1020; ^{1}HNMR (400 MHz, DMSO–d$_6$): δ 8.49–8.27 (m, 3H), 8.2 (d, *J* = 5.6 Hz, 1H), 7.74 (m, 3H), 6.82 (s, 2H), 4.76 (s, 3H), 3.72–3.62 (m, 4H), 3.48–3.35 (m, 4H); MS (EI) m/z: 314.1 (M+1).

3.2.3. BET Surface area analysis

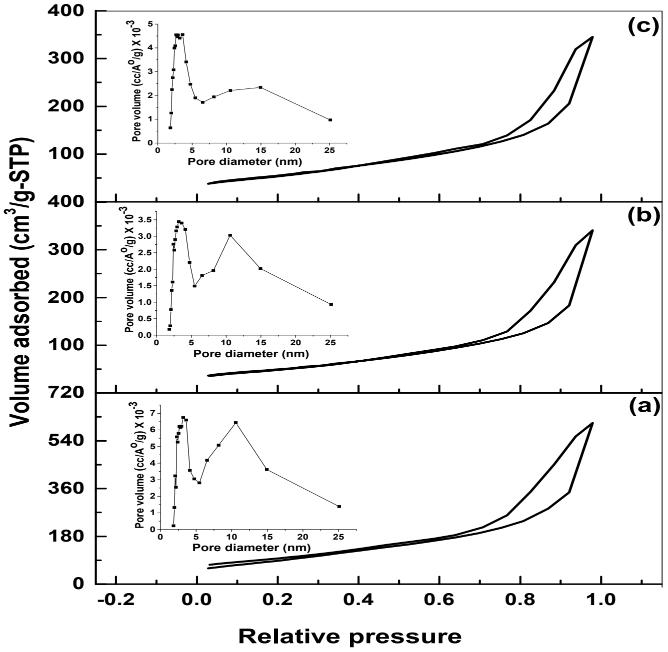


Fig. S13. N_2 adsorption-desorption isotherm and corresponding pore size distributions of the a) F/MWCNT, b) Cu-Ru/MWCNT and c) Cu-Ni/MWCNT catalysts.

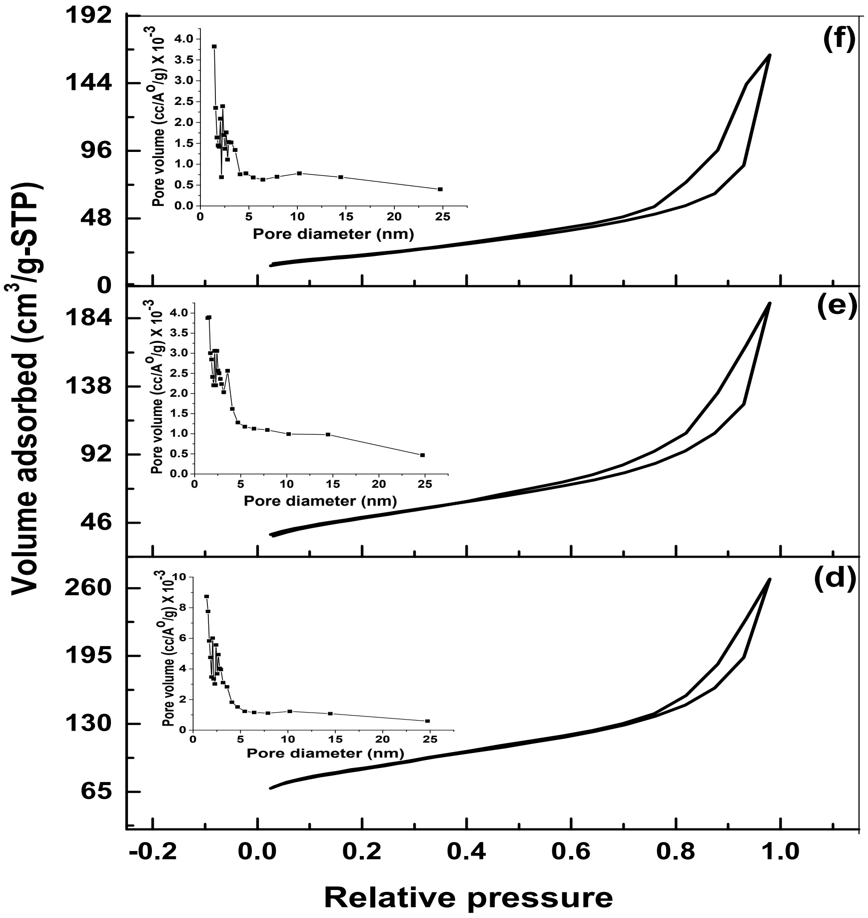
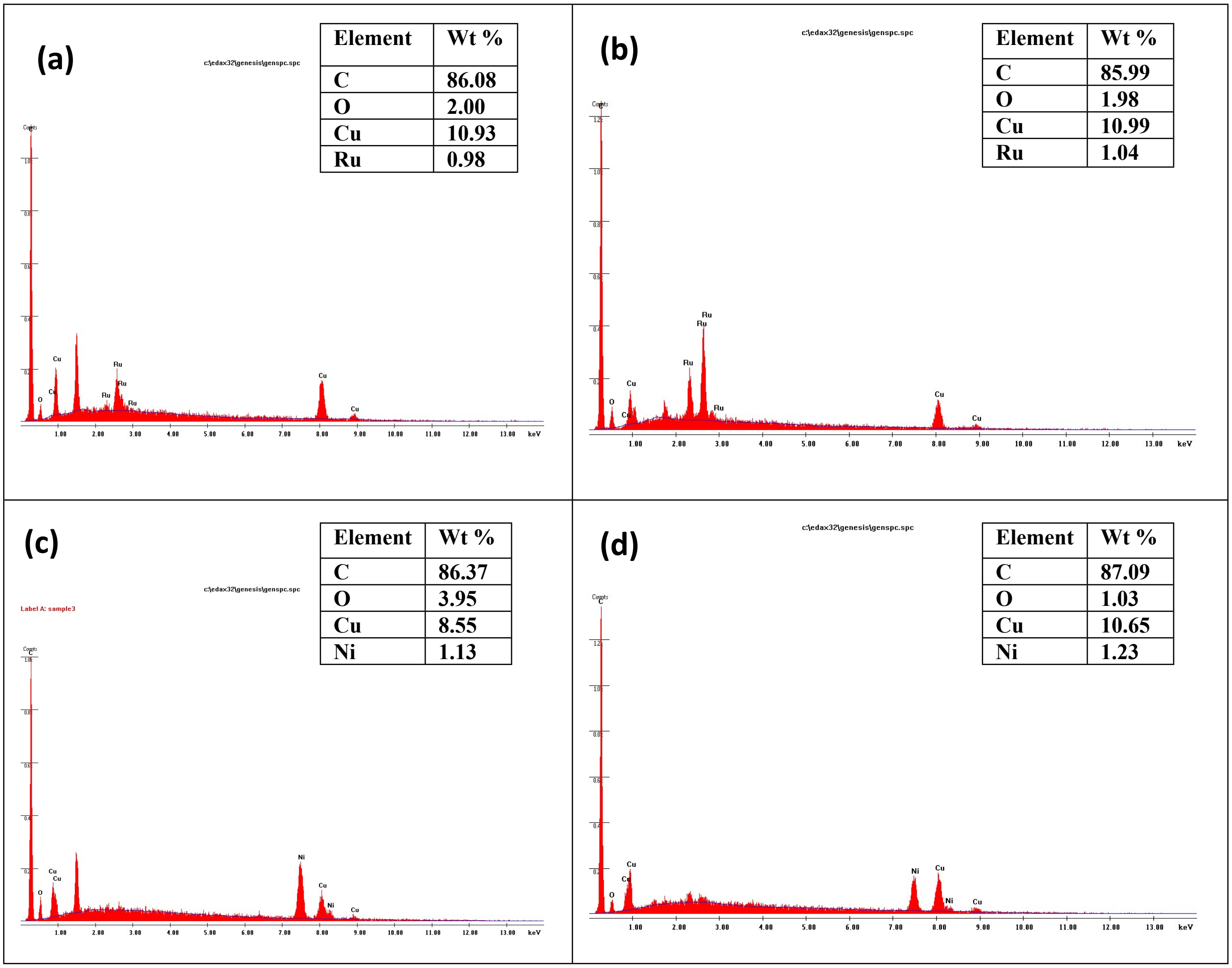


Fig. S14. N_2 adsorption-desorption isotherm and corresponding pore size distributions of the d) F/MC, e) Cu-Ru/MC and f) Cu-Ni/MC catalysts.



(a)

Element	Wt %
C	86.08
O	2.00
Cu	10.93
Ru	0.98

(b)

Element	Wt %
C	85.99
O	1.98
Cu	10.99
Ru	1.04

(c)

Element	Wt %
C	86.37
O	3.95
Cu	8.55
Ni	1.13

(d)

Element	Wt %
C	87.09
O	1.03
Cu	10.65
Ni	1.23

Fig. S15. EDS profile of (a) Cu-Ru/MWCNT, (b) Cu-Ru/MC, (c) Cu-Ni/MWCNT and (d) Cu-Ni/MC catalysts.

Supplementary table (ST)

ST-1. Reduction of 4-bromo nitrobenzene over Cu-Ru/MWCNT catalyst in presence of different Lewis acids.

Entry	Catalyst	Lewis acids	Selectivity % X (XI) (Other)	% Yield (X)
1	No Catalyst	Anhydrous $CoCl_2$	100 (0) (0)	8
2	Cu-Ru/MWCNT	Anhydrous $CoCl_2$	93 (7) (0)	75
3	Cu-Ru/MWCNT	Anhydrous $FeCl_2$	89 (11) (0)	64
4	Cu-Ru/MWCNT	Anhydrous $ZnCl_2$	82 (15) (3)	58
5	Cu-Ru/MWCNT	Anhydrous $FeCl_3$	78 (19) (3)	52
6	Cu-Ru/MWCNT	Anhydrous $SnCl_2$	74 (20) (6)	50
7	Cu-Ru/MWCNT	Anhydrous $AlCl_3$	60 (32) (8)	43

Reaction Conditions: *1 mmol of 4-bromo nitro benzene, 0.1 g of catalyst Cu-Ru/MWCNT, 0.5 mmol of Lewis acid, H_2 1 atm, 20 mL ethanol: water (9:1) solvent, 2 h.*

ST-2. Surface properties of the catalyst.

Entry	Catalyst	BET Surface Area ($m^{2/}g$)	Pore volume (cm^3/g)	Pore Size (nm)
1	F/MWCNT	333.04	0.85	10.3
2	Cu-Ru/MWCNT	175.83	0.47	9.73
3	Cu-Ni/MWCNT	199.43	0.49	9.90
4	F/MC	290.12	0.35	4.91
5	Cu-Ru/MC	162.90	0.22	3.90
6	Cu-Ni/MC	169.73	0.25	4.33