



**Environmentally Benign Selective Hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes and Reduction of Aromatic Nitro Compounds using Cu Based Bimetallic Nanoparticles Supported on Multiwalled Carbon Nanotubes and Mesoporous Carbon**

Journal:	<i>RSC Advances</i>
Manuscript ID	RA-ART-02-2016-004241.R2
Article Type:	Paper
Date Submitted by the Author:	05-Jul-2016
Complete List of Authors:	Nagaraju, Hareesh; Jain University, C.E.T Raghavendra, Minchitha; Jain University, C.E.T Venkatesh, Krishna; Jain University N., Nagaraju; St. Joseph's college, Bangalore, Chemistry Nagaraju, Kathyayini; Jain University, CET
Subject area & keyword:	Heterogeneous < Catalysis

# Environmentally Benign Selective Hydrogenation of $\alpha$ , $\beta$ -unsaturated aldehydes and Reduction of Aromatic Nitro Compounds using Cu Based Bimetallic Nanoparticles Supported on Multiwalled Carbon Nanotubes and Mesoporous Carbon

Hareesh H. N<sup>1,2</sup>, Minchitha K.U<sup>1</sup>, Venkatesh K<sup>1</sup>, Nagaraju N<sup>3</sup>, Kathyayini N<sup>1\*</sup>

<sup>1</sup>Centre for Incubation, Innovation Research and Consultancy, A Joint Initiative of Sri Sharada Peetham, Sringeri & Jyothy Institute of Technology Campus, Tataguni off Kanakapura Road, Bengaluru – 560082, Karnataka, India.

<sup>2</sup>Visvesvaraya Technological University - Research Resource Centre, Jnana Sangama, Belagavi – 590018, Karnataka, India.

<sup>3</sup>Department of Chemistry, St. Joseph's College P.G. Centre, 46, Langford Road, Shanthinagar, Bengaluru – 560027, Karnataka, India.

(\*) corresponding author: E-mail address: nkathyayini45@gmail.com, Mobile: 9886506387, Fax: +91 80 27577211

## Abstract:

Bimetallic catalysts of Cu with Fe, Co, Ni, Zn or Ru supported on multiwalled carbon nanotubes (MWCNT) and mesoporous carbon (MC) were prepared by in situ reduction of CuCl<sub>2</sub> and the metal chlorides using NaBH<sub>4</sub>. The catalytic activity of these materials was investigated in the hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes and reduction of aromatic nitro compounds using different hydrogen sources. Cu-Ni and Cu-Ru supported on MWCNT catalysts were found to be better than MC supported catalysts in terms of yield of the expected product and recyclability. Among the different hydrogen sources used molecular H<sub>2</sub> was found to be the best for the hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes to corresponding alcohols (conversion 83–86 %, selectivity 72–78 %), whereas NaBH<sub>4</sub> was the best for the reduction of aromatic nitro compounds to corresponding amines (conversion 100 %, selectivity 98 %). The reaction conditions were optimised for good yield and selectivity of the product. Generality of the catalysts was also investigated in the reduction of different  $\alpha$ ,  $\beta$ -unsaturated aldehydes and aromatic nitro compounds. Relationship between catalytic activity and physico-chemical

properties was investigated by characterising the catalytic materials by Powder X-ray diffraction (Powder XRD), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area, Scanning electron microscopy (SEM) - Energy Dispersive X-ray spectroscopy (EDS) and Transmission electron microscopy (TEM).

*Keywords:* Bimetallic nanoparticles, Hydrogenation,  $\alpha$ ,  $\beta$ - unsaturated aldehydes, nitro compounds.

## 1. Introduction

Heterogeneous catalysis plays a pivotal role in the reduction of environmental pollution. In this regard the main objectives of heterogeneous catalysis are (a) application of mild reaction conditions (b) usage of eco-friendly solvents (c) prevention of hazardous and toxic wastes (d) development of recyclable catalysts and (e) formation of products with high percentage yield and selectivity.<sup>1-3</sup> In heterogeneous catalysis porous solids are used as supports for the uniform dispersion of the active metal or metal oxide catalysts and further to reduce the cost of the active catalyst. In several instances the supported catalysts exhibited improved catalytic activity.<sup>4-6</sup> Recently, multiwalled carbon nanotubes (MWCNT) and mesoporous carbon (MC) are used as catalyst supports due to their (i) well-defined and tunable structures (ii) high catalytic activities arising from their mesoporosity (iii) ability to avoid mass transfer limitations and (iv) high surface area available for the uniform dispersion of active catalyst.<sup>7-9</sup>

Selective hydrogenation of C=C bond of  $\alpha$ ,  $\beta$ -unsaturated aldehydes result corresponding unsaturated alcohols, which find applications as intermediates in flavors, fragrance and pharmaceuticals.<sup>10-12</sup> It is a known fact that C=C bond is more susceptible to hydrogenation than the C=O bond.<sup>13, 14</sup> Low-cost Cu-based materials are employed as catalysts in industry for selective hydrogenation of C=O bond in carbonyl compounds. It is noticed that a synergetic effect of  $\text{Cu}^+/\text{Cu}^0$  in Cu-based catalysts remarkably control the catalytic performance in the hydrogenation of carbonyl compounds.<sup>10, 15-17</sup>

Ni, Pd, Pt, Ru and Pt-Ru catalysts supported on CNTs and Cu supported on mesoporous carbon are investigated for their catalytic activity in the hydrogenation of  $\alpha$ ,  $\beta$ - unsaturated aldehydes, but the selectivity and % yield of the product were found to be low and the catalysts are expensive.<sup>18-21</sup> Hence development of low cost and efficient catalysts for the selective hydrogenation of conjugated aldehydes without effecting to C=C bond to the corresponding

unsaturated alcohol is a challenging and significant task, from both academic and industrial point of view.

Similarly, the selective reduction of a nitro group in the presence of other labile groups in an aromatic compound is an industrially important organic transformation in the preparation of amines, which in turn are used in the synthesis of many agrochemicals, pharmaceuticals, dyes, rubbers, polymers and pigments.<sup>22, 23</sup> Supported noble metals and their compounds are investigated for their catalytic activity in the selective reduction of nitro group.<sup>24-26</sup> However the amount of the noble metals used in the case of supported catalysts is quite high and hence the process is expensive. Further these methods also have some draw-backs such as long reaction time and water sensitivity of the reagents. Further, selective reduction of various aromatic nitro compounds using Cu and Ni nanoparticles based catalysts, as well as the promotional effect of Cu in bimetallic catalyst with respect to the stability and selectivity has been discussed.<sup>27-33</sup>

It is also evident from the reported literature that Cu based catalysts along with the noble metals are suitable catalytic materials for hydrogenation/reduction reactions. In this present investigation we have explored the possibility of using very low percentage of noble metal along with inexpensive Cu to develop bimetallic catalysts with good selectivity and yield for the title reactions. We have also made an attempt to correlate the structure-catalytic activity of the material by suitable characterization techniques.

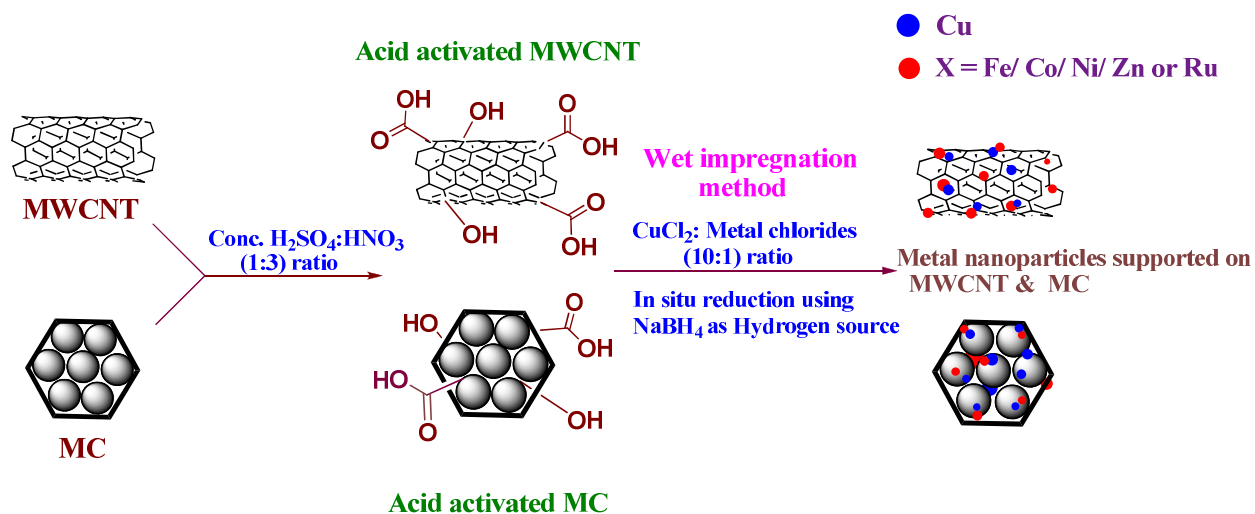
## **2. Experimental**

### **2.1. Preparation and characterization of MWCNT and MC supported single and bimetal catalysts:**

Multiwalled carbon nanotubes (MWCNT) were purchased from Reinste Nano ventures Pvt. Ltd and Mesoporous carbon (MC) from Sigma Aldrich. The Powder XRD patterns, SEM –EDS and TEM images of these materials are given as SI (S1, S2 and S3).

MWCNT and MC materials were activated by Conc. HNO<sub>3</sub> and Conc. H<sub>2</sub>SO<sub>4</sub> (1:3). The materials thus obtained were abbreviated as F/MWCNT (Functionalized multiwalled carbon nanotubes) and F/MC (Functionalized mesoporous carbon). Further, these functionalized materials used as supports for the preparation of monometal and bimetal containing catalysts by reduction method, using NaBH<sub>4</sub> as a reducing agent.<sup>34</sup> The experimental details of catalysts

preparation are given in SI. Preparation of acid activated MWCNT/MC and the metal ion supported carbon material is pictorially represented in Scheme 1. All the prepared materials were characterized by Powder XRD, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area, SEM-EDS and TEM techniques.

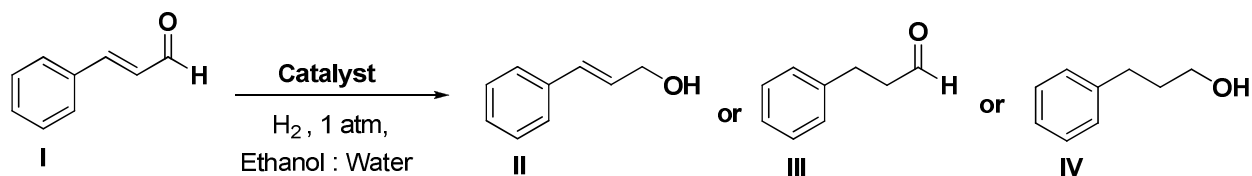


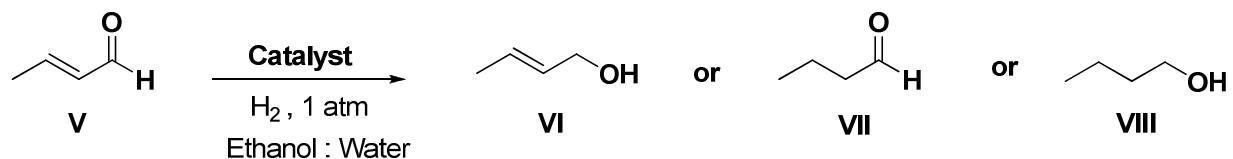
**Scheme 1.** Schematic representation of synthesis of metal/s nanoparticles supported on F/MWCNT and F/MC.

### 3. Results and Discussion

**3.1. Catalytic activity studies:** Catalytic activity of the prepared materials was investigated in the selective hydrogenation of C=O bond of  $\alpha$ ,  $\beta$ -unsaturated aldehydes (Cinnamaldehyde and Crotonaldehyde) and reduction of nitro group in an aromatic compounds under refluxing conditions. The experimental details of the reactions are included in SI.

**a. Hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes:** The expected hydrogenation products of Cinnamaldehyde and Crotonaldehyde are presented in the reaction scheme 2.





**Scheme 2.** Hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes in the presence of Cu/X/ MWCNT or Cu/X/MC as catalysts (X = Fe/ Co/ Ni/ Zn or Ru).

Initially it was noticed that acid activated MWCNTs/MC, single metal and bimetal supported carbon materials, except Cu-Ru and Cu-Ni catalysts, did not show any significant catalytic activity in the hydrogenation of **I** and **V** into any of the expected products. Further, MWCNT/MC supports containing 1 % of Fe, Co and Zn were also catalytically inactive did not show any catalytic activity, whereas those containing 1 % of Ni or Ru metals showed activity to an extent of only 10 % conversion of the **I** and **V** aldehydes into the corresponding alcohols (**II** and **VI**). The catalyst with 10 % Cu exhibited a slightly better activity (10–14 % conversion) than Ni and Ru incorporated materials. These results prompted to check the effect of combining Cu with other transition metals on their catalytic activity in the hydrogenation of **I** and **V**. Bimetallic compositions with 10 % Cu and 1 % of Fe, Co, Zn showed slightly increasing in catalytic activity (20–28 % conversion) than the catalyst with only Cu but a combination of 10 % Cu and 1 % Ni or Ru exhibited very significant rise in the catalytic activity in the hydrogenation of  $\alpha,\beta$  unsaturated aldehydes. Further, the % conversions of **I** and **V** as well as the selectivity towards alcohol products (**II** and **VI**) were much higher with Cu-Ru than Cu-Ni catalyst. The results are presented in table 1 (entries 3, 4, 5 and 6). It is also interesting to note that the selectivity of the product **II** and **VI** depends further on the type of the carbon support used.

In the hydrogenation of cinnamaldehyde (**I**), Cu-Ru/MWCNT showed higher conversion (83 %) and selectivity (78 %) towards **II**, cinnamyl alcohol, than Cu-Ru/MC for which these values were respectively 80 % and 60 %. Similarly, in the hydrogenation of **V**, 86 % conversion and 72 % selectivity for **VI**, was noticed in the presence of Cu-Ru/MWCNT catalyst. However, Cu-Ru/MC catalyst showed 89 % conversion and selectivity only 63 % for the alcohol. The difference in the selectivity's between the MWCNT/MC supported catalysts is attributed to the difference in BET surface area and surface morphology associated with their mesoporous structure and hence the metal support interactions. These characteristic properties of the materials are presented in the later part of discussion in this paper. It was noticed that, in

presence of Cu-Ni/MWCNT and Cu-Ni/MC catalyst, the % conversion of the aldehydes was in the range 40–53, whereas the selectivity for the corresponding alcohols was in the range 45–52. These values are thus much lower than those for Cu-Ru catalysts supported on the same carbon materials.

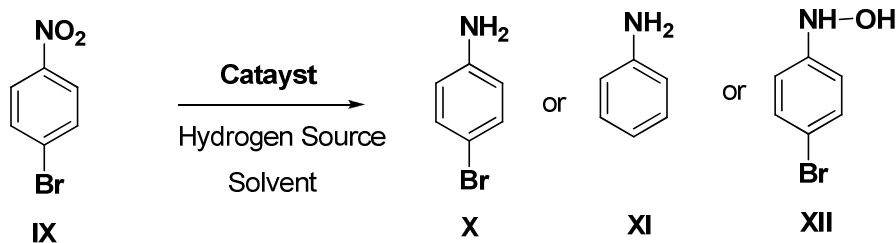
The correlation between the selectivity for unsaturated alcohol (**II** and **VI**) and the ratio of  $\text{Cu}^+/\text{Cu}^0$  in Cu-Ru and Cu-Ni catalyst supported on carbon materials is notable. It is reported that  $\text{Cu}^+$  sites are responsible for the selective hydrogenation of C=O bond. A higher ratio of  $\text{Cu}^+/\text{Cu}^0$  leads to higher selectivity for **II** or **VI**, unsaturated alcohols. This is consistent with the Powder XRD and XPS results on these materials discussed later in this paper. Gong, J et al., have reported that,  $\text{Cu}^0$  species are associated with both decomposition of molecular hydrogen as well as reduction of C=C double bond, whereas  $\text{Cu}^+$  species are selective in the hydrogenation of C=O double bond.<sup>10</sup> Thus an increase in the  $\text{Cu}^+$  species in the catalyst would increase the selectivity for unsaturated alcohol. It is understood from the literature that, the presence of Au or Ru along with  $\text{Cu}^0$ , increases the later activity for molecular hydrogen decomposition. This increases the overall activity and selectivity for the unsaturated alcohol in the presence of Cu-Ru catalysts. In the case of Cu-Ni catalyst the lower selectivity for unsaturated alcohol can thus be attributed not only to higher concentration of  $\text{Cu}^0$  species but also to the lower catalytic activity of Ni species for molecular hydrogen decomposition.<sup>10, 12, 35</sup>

**Effect of the nature of hydrogen sources:** As Cu-Ru/MWCNT catalyst showed better activity in terms of selectivity for unsaturated alcohols, further studies on the effect of the nature of the hydrogen sources are investigated. The results concerning these studies in the hydrogenation of cinnamaldehyde and crotonaldehyde by Cu-Ru/MWCNT catalyst are presented in the table 2.

The selected reducing agents are known to generate molecular hydrogen through catalytic decomposition over metal/metal oxide surfaces, and due to their intrinsic difference in their chemical reactivity the extent of their reaction alters with the nature of the metal.<sup>36–39</sup>

### **b. Reduction of aromatic nitro compounds**

Initially Cu/X/MWCNT or Cu/X/MC catalysts (where X = Fe/ Co/ Ni/ Zn or Ru) were investigated for their catalytic activity in the reduction of 4-bromo nitrobenzene (Table 3). The expected products of reduction of 4-bromo nitrobenzene are presented in the reaction scheme 3.



**Scheme 3.** Reduction of 4-bromo nitrobenzene in the presence of Cu/X/MWCNT or Cu/X/MC catalysts (X = Fe/ Co/ Ni/ Zn or Ru).

Initially a reaction was conducted using H<sub>2</sub> gas in the presence of plain acid activated carbon materials and 0.5 mmol of anhydrous CoCl<sub>2</sub>. These materials did not show any catalytic activity in the reduction of **IX** into any of the expected products (**X–XII**) (Table 3, entries 1 & 2). However, single metal supported carbon materials (1 % of Fe, Co and Zn) exhibited very low catalytic activity (< 6 % conversion), whereas, 1 % of Ni and Ru metals showed slight increase in activity (10–15% conversion) of 4-bromo nitrobenzene to 4-bromoaniline (**X**). Further, the materials with 10 % Cu exhibited a slightly better activity (18–20 % conversion).

From these results, the effect of combining Cu with other transition metals on their catalytic activity in the reduction of 4-bromo nitrobenzene was evaluated. Bimetallic compositions with 10 % Cu and 1 % of Fe, Co and Zn showed slight increase in catalytic activity (conversion 40–45 %) than 10 % Cu catalyst. Noteworthy that, combination of 10% Cu and 1% Ni or Ru, exhibited a significant rise in the catalytic activity in the reduction of 4-bromo nitrobenzene. It was further noticed that % conversions of 4-bromo nitrobenzene (**IX**) as well as the % selectivity and yield towards 4-bromoaniline (**X**) were much higher with Cu-Ru than Cu-Ni catalysts supported on carbon materials. The results are presented in table 3 (entries 9, 10, 11 and 12). It is also to be noted that the selectivity of **X** depends further on the type of the carbon support.

In comparison with all the catalysts mentioned in table 3, Cu-Ru/MWCNT showed improved catalytic activity and selectivity towards the formation of 4-bromoaniline in presence of molecular H<sub>2</sub> and CoCl<sub>2</sub>.

**Role of Lewis acid:** Under the same reaction conditions, the catalytic reduction of 4-bromo nitrobenzene was conducted in the presence of Cu-Ru/MWCNT catalyst with different Lewis acids like FeCl<sub>3</sub>, FeCl<sub>2</sub>, AlCl<sub>3</sub>, ZnCl<sub>2</sub> and SnCl<sub>2</sub> results are presented in supplementary table (ST-



1). High yield and good selectivity of 4-bromoaniline (**X**) was obtained with weak Lewis acids like  $\text{CoCl}_2$  and  $\text{FeCl}_2$  whereas, strong Lewis acids like  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$  and  $\text{AlCl}_3$  gave less yield and selectivity of **X**, due to their high reactivity with nitro compound. However, in presence of  $\text{CoCl}_2$  and  $\text{FeCl}_2$  no debromination product (**XI**) was observed, but in presence of  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$  and  $\text{SnCl}_2$ , up to 26 % of debromination product was observed. This indicates the existence of strong synergetic effect between Lewis acid and Cu-Ru/MWCNT catalyst.

A plausible reaction mechanism for the reduction of 4-bromo nitrobenzene over Cu-Ru/MWCNT with  $\text{H}_2$  was proposed based on the reported literature by Z. Zhao et al.,<sup>41</sup> is shown in supplementary data Fig. S8. It is reported that, Zero valent metal nanoparticles ( $\text{Cu}^0$ ,  $\text{Ni}^0$  and  $\text{Ru}^0$ ) present on the support activate  $\text{H}_2$  to produce active H for the reaction and Lewis acid activate aromatic  $\text{NO}_2$  group for hydrogenation by weakening  $\text{NO}_2$ ,  $\text{N}=\text{O}$  and  $\text{N}-\text{O}$  bonds through its electron accepting properties. Possible steps involved in the hydrogenation is as follows: (i) Formation of active hydrogen over catalyst surface, (ii)  $\text{N}-\text{O}$  of  $\text{NO}_2$  is activated by the coordination of catalyst with N atom and the Lewis acid with O, and then activated H interacts with the activated  $\text{N}-\text{O}$  bond, and thereby formation of intermediate 1-bromo 4-nitrosobenzene (**A**), with the elimination of  $\text{H}_2\text{O}$  molecule (iii) Further, the 1-bromo 4-nitrosobenzene (**A**) is reduced with  $\text{H}_2$  to N-(4-bromophenyl) hydroxyl amine intermediate (**B**). Similarly, intermediate '**B**' is further activated and reduced to produce the 4-bromoaniline (**X**).

**Effect of the nature of hydrogen sources:** The catalytic activity of Cu-Ru/MWCNT catalyst was also investigated using different hydrogen sources such as  $\text{NaBH}_4$ , Hydrazine hydrate, Formic acid and Acetic acid. It is interesting to note that the % conversion of **IX**, selectivity and yield of **X** were respectively 90, 93 and 75 (Table 5 entry 1) in a reaction carried out for 2 h at  $100^\circ\text{C}$  using  $\text{H}_2$  as a reducing agent where as these numbers not only increased significantly but also obtained under much milder reaction conditions (RT, 30 min) with  $\text{NaBH}_4$  and  $\text{NH}_2\text{NH}_2$  as reducing agents table 4 (entries 2 & 3). However, formic acid and acetic acid showed very low conversions table 4 (entries 4 & 5).

A plausible reaction mechanism for the reduction of aromatic nitro compounds to corresponding amine using Cu-Ru/MWCNT catalyst with  $\text{NaBH}_4$  as hydrogen source showed in Fig. 1. The mechanism was proposed based on the reported literature.<sup>42</sup> The reduction of nitro compound

involves electron transfer from  $[\text{BH}_4]^-$  ion to the nitro compound through the catalyst. Thereby larger amount of hydride can be transferred or a larger amount of  $\text{H}_2$  gas can be produced in the reduction of nitro compound.

### **Optimization of the reaction conditions and recyclability studies using Cu-Ru/MWCNT and Cu-MC catalysts**

The effect of solvent, temperature and duration of the reaction as well as amount of the catalyst was investigated in the hydrogenation of cinnamaldehyde and reduction of 4-bromo nitrobenzene using Cu-Ru/MWCNT as the catalyst to get the best yield and selectivity of the cinnamyl alcohol and 4-bromo aniline respectively. The results are given as supplementary data in Fig. S4 – S12. A maximum yield of the expected products was obtained in ethanol and water (9:1) mixture for both the reactions but at 100 °C for hydrogenation and room temperature for reduction reaction. 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  $\text{H}_2$  in polar solvents.<sup>16, 40</sup>

Cu-Ru/MWCNT catalyst was found to be recyclable up to 5 times without any alteration in its, selectivity for the expected products II and X (Fig. S7 & S12 (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 & S12 (b)). The recyclability of the catalysts demonstrates Cu and Ru species are the catalytic active sites dispersed over carbon supports that play a synergetic role in this reaction.

### **Generality of Cu-Ru/MWCNT catalyst in the reduction of aromatic nitro compounds**

Several substituted aromatic nitro compounds were subjected in the reduction reactions using Cu-Ru/MWCNT catalyst in presence of  $\text{NaBH}_4$  as hydrogen source. The results are presented in table 5 and 6. 4-Chloro and 4-bromo nitrobenzene (entries 5 and 6, Table 5) were completely reduced to the corresponding anilines without any dehalogenation, which was often encountered with several hydrogenation reactions.<sup>22, 43</sup> 4-cyano nitrobenzene (entry 10, Table 5) was reduced

to 4-cyano aniline keeping the -CN group intact. The ketocarbonyl and carboxylic functionalities present in the aromatic ring also remained unaffected during reduction of the corresponding nitrobenzenes by employing Cu-Ru/MWCNT catalyst (entries 9 & 12, Table 5). To extend the scope of the catalyst various heterocyclic aromatic nitro compounds are also reduced to corresponding amines using Cu-Ru/MWCNT catalyst (Table 6). Spectroscopic data of the some heterocyclic compounds reported in Table 6 are presented in supplementary data (SD-1).

### 3.2. Characterization of the catalysts

**3.2.1. Powder XRD:** Cu-Ru/MWCNT and Cu-Ni/MWCNT catalysts graphitic structure of MWCNT ( $25.96^\circ$  and  $43.49^\circ$ ), fcc metallic Cu ( $43.3^\circ$ ,  $50.42^\circ$  and  $74.1^\circ$ , JCPDS no. 04–0836) and cubic phases of  $\text{Cu}_2\text{O}$  ( $36.3^\circ$  and  $61.4^\circ$ , JCPDS no. 78–2076) on MWCNT are evident from the powder XRD patterns (Fig. 2a, b, c).<sup>44–47</sup> The diffraction peaks of metallic Ru ( $2\theta = 42.2^\circ$  and  $69.4^\circ$ )<sup>48</sup> and metallic Ni are very weak because of low percentage loading (1 %) of Ru or Ni in the corresponding catalysts. Similarly, Cu-Ru/MC and Cu-Ni/MC catalysts hexagonal graphitic structure of carbon<sup>49</sup>, fcc metallic copper and cubic phases of  $\text{Cu}_2\text{O}$  were observed on MC. The diffraction peaks at metallic Ru ( $42.17^\circ$  and  $78.33^\circ$ ) and metallic Ni ( $44.7^\circ$  and  $76.27^\circ$ , JCPDS no. 87–0712)<sup>42, 50</sup> are evident from the corresponding powder XRD patterns (Fig. 2e, f, g).

Powder XRD studies indicated the presence of metallic Cu as well as  $\text{Cu}_2\text{O}$  on the supported carbon materials. Further, indicated that the MWCNT did not lose their graphitic structure. The intensities of the diffraction peaks due to metallic Cu in Cu-Ni catalysts were more than in Cu-Ru. On the other hand the intensities of the peaks due  $\text{Cu}_2\text{O}$  is reverse. These results clearly indicate why selectivity of cinnamyl alcohol is more in case of Cu-Ru supported catalyst than Cu-Ni catalyst.

**3.2.2. XPS Analysis:** XPS characterization of materials provides information regarding oxidation state of the copper species associated with the catalysts under investigation. These studies are useful in evaluating the role copper species ( $\text{Cu}^0/\text{Cu}^+$ ) which contribute towards catalytic activity. The XPS spectra of Cu  $2p_{3/2}$  and  $2p_{1/2}$  electrons for Cu, Cu-Ru and Cu-Ni supported on MWCNT/MC catalyst are depicted in Fig. 3. The binding energies (B.E) of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  electrons in Cu/MWCNT & Cu/MC are 932.4 eV and 952.3 eV respectively, indicating the presence of both metallic  $\text{Cu}^0$  and  $\text{Cu}^+$  species (Table 7). However, in bimetallic

catalysts the B.E are shifted to higher values indicating that there is a strong interaction of Cu with Ru/Ni.<sup>51–53</sup>

Further an analysis of XPS spectra of C (1s) electron in Cu and bimetallic catalysts deposited on MWCNT and MC (Table 7) revealed the difference in the interaction of the metallic species with the support. For instance the B.E of C1s electron in Cu/MWCNT was found to be 284.8 eV, and this value is shifted in Cu-Ru and Cu-Ni catalysts supported on MWCNT indicating a noticeable surface interactions.<sup>52, 53</sup> On contrary to this, the BE of C1s electron in MC supported catalysts remained unchanged. These results corroborate with the recyclability of these catalysts in hydrogenation and reduction reactions. Due to higher interaction between the support and the metallic particles in MWCNT based catalysts than in MC supported catalysts the former catalysts are efficiently recyclable.

**3.2.3. BET Surface area:** In both MWCNT and MC catalysts the BET surface area, pore volume and pore diameter decreased significantly upon incorporation of bimetallic species (Cu-Ru and Cu-Ni) into functionalized carbon materials (ST-2, entry 2, 3 and 5, 6). The N<sub>2</sub> adsorption-desorption isotherms indicated a mesoporous structure of the materials.<sup>18, 54, 55</sup> with pore diameters 3.2 and 10.6 nm. (Fig. S13 & S14).

**3.2.4. SEM-EDS:** Fig. 4a and 4c represents SEM images of Cu-Ru/MWCNT and Cu-Ni/MWCNT, indicates the presence of small metal particles deposited over the mesoporous tubular structured MWCNT. Similarly, in the case of MC based catalysts which are obtained as carbon spheres, small metal nanoparticles were also observed on the surface of their pores. The EDS profiles of the catalytic materials are included in SI (Fig.S15) which gives the atomic percentages of carbon, oxygen, copper, ruthenium and nickel. The atomic percentages of the metals deposited on MWCNT and MC as mentioned in the corresponding EDS profiles are also matching with the amount of metals deposited during synthesis procedure.

**3.2.5. TEM Analysis:** Fig. 5 & 6 represents TEM images of Cu-Ru/MWCNT, Cu-Ru/MC, Cu-Ni/MWCNT and Cu-Ni/MC. It is clear from Fig. 5 (a-d), metal nanoparticles are deposited on inner and outer walls of MWCNT. In the case of Cu-Ru/MWCNT, irregular shaped metal nanoparticles are deposited on MWCNT, while in Cu-Ni/MWCNT hexagonal shapes of metal nanoparticles were noticed on outer walls of MWCNT. However, the density of metal

nanoparticles deposited on Cu-Ni/MWCNT was found to be greater than in the case of Cu-Ru/MWCNT. Similarly, in Cu-Ru/MC and Cu-Ni/MC catalysts, metal/s nanoparticles are observed on the surface of the mesoporous carbon spheres as dark spots (Fig. 6e-h).

#### 4. Conclusion

In summary, Cu based bimetallic catalysts supported on mesoporous MWCNT and MC were synthesized *via* wet impregnation method. The resultant catalysts were tested in hydrogenation of  $\alpha$ ,  $\beta$  unsaturated aldehydes and reduction of nitroarenes. Cu-Ru/MWCNT catalyst containing only 1 % noble metal was found to be an excellent and selective catalyst for the hydrogenation of  $\alpha$ ,  $\beta$  unsaturated aldehydes as well as reduction of aromatic nitro compounds. Cu-Ru/MWCNT catalyst containing only 1 % noble metal exhibited good selectivity for the unsaturated alcohol formation in the range of 72–78 %. A synergistic effect between Cu and Ru was proposed. Ru sites were responsible for the dissociative activation of H<sub>2</sub> molecules and Cu<sup>+</sup> sites contribute on adsorption-activation of C=O bond and produced unsaturated alcohol. Similarly, in the reduction of aromatic nitroarenes Cu-Ru/MWCNT found to be efficient catalyst to reduce wide variety of nitroarenes with NaBH<sub>4</sub> as the hydrogen source. This catalyst is more selective to –NO<sub>2</sub> group and unaffected to the other sensible functional groups (-Br, -Cl or -CN). Further, catalyst can be recyclable upto 5 times without loss of its catalytic activity.

#### Acknowledgement

The authors thank DST–SERB for the financial support given for this research work. Project Number: SERB/F/3690/2013–14. Authors thank Dr. Chenraj Roychand, President Jain University trust for their constant support in encouraging this research work.

#### References

1. M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.*, 2011, **111** (2), 1072–1133.
2. Guibal. E, *Prog. Polym. Sci.*, 2005, **30**, 71–109.
3. T. K. Hari and Z. Yaakob, *Chin. J. Chem. Eng.* 2014, DOI: 10.1016/j.cjche.2014.01.002
4. H. U. Blaser, *Catalysis Today*, 2000, **60**, 161–165.

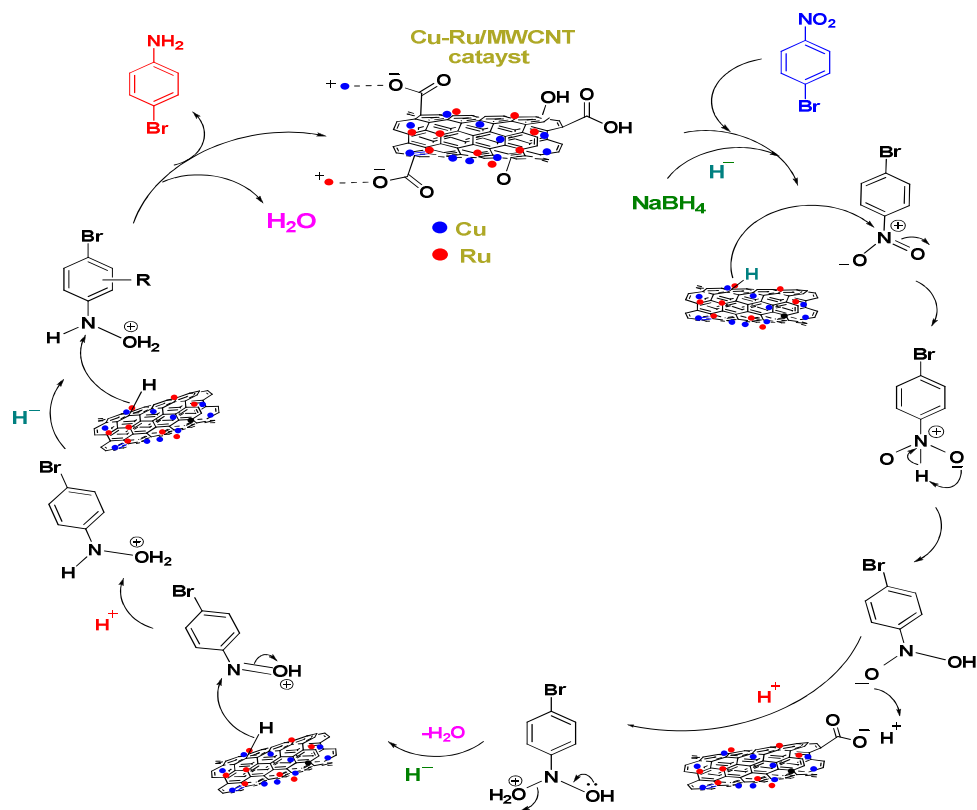
5. K. T. Lee, X. Ji, M. Rault, and L. F. Nazar, *Angew. Chem.* 2009, **121**, 5771–5775.
6. A. Eatemadi, H. Daraee, H. Karimkhanloo, M. Kouhi, N. Zarghami, A. Akbarzadeh, M. Abasi, Y. Hanifehpour, and S. W. Joo, *Nanoscale Res. Lett.*, 2014, **9**, 393–405.
7. D. Eder. *Chem. Rev.*, 2010, **110 (3)**, 1348–1385.
8. A. Stein, Z. Wang and M. A. Fierke, *Adv. Mater.*, 2009, **21**, 265–293.
9. H. N. Hareesh, K. U. Minchitha, N. Nagaraju and N. Kathyayini, *Chin. J. Catal.*, 2015, **36**, 1825–1836.
10. X. Yuan, J. Zheng, Q. Zhang, S. Li, Y. Yang and J. Gong, *Am. Ins. Chem. Eng (AIChE)*, DOI: 10.1002/aic.14522
11. B. Li, G. S. Hu, L. Y. Jin, X. Hong, J. Q. Lu and M. F. Luo, *J. Ind. Eng. Chem.*, 2013, **19**, 250–255.
12. A. J. Marchi, D. A. Gordo, A. F. Trasarti and C. R. Apesteguia, *Appl. Catal., A*, 2003, **249**, 53–67.
13. J. Shi, R. Nie, P. Chen and Z. Hou, *Catal. Commun.*, 2013, **41**, 101–105.
14. H. Rojas, G. Diaz, J. J. Martinez, C. Castaneda, A. G. Cortes, J. A. Alatorre, *J. Mol. Catal. A*, 2012, **363–364**, 122–128.
15. V. S. Gutierrez, A. S. Diez, M. Dennehy and M. A. Volpe, *Microporous and Mesoporous Materials*, 2011, **141**, 207–213.
16. H. Liu, Q. Hu, G. Fan, L. Yang, and F. Li, *Catal. Sci. Technol.*, 2015, **5**, 3960–3969. DOI: 10.1039/C5CY00437C.
17. W. Li, G. Fan, L. Yang and F. Li, *Catal. Sci. Technol.*, 2016, **6**, 2337–2348.
18. Z. Liu, Y. Yang, J. Mi, X. Tan and Y. Song, *Catal. Commun.*, 2012, **21**, 58–62.
19. H. Vu, F. Goncalves, R. Philippe, E. Lamouroux, M. Corrias, Y. Kihn, D. Plee, P. Kalck and P. Serp, *J. Mol. Catal. A: Chem.*, 2006, **240**, 18–22.

20. M. Jahjah, B. Caron, S. Menuel, E. Monflier, L. Djakovitch and C. Pinel, *ARKIIOC*, 2011, **7**, 406–415.
21. C. Mohr, H. Hofmeister, J. Radnik and P. Claus, *J. Am. Chem. Soc.*, 2003, **125**, 1905–1911.
22. A. Saha and B. Ranu, *J. Org. Chem.*, 2008, **73**, 6867–6870.
23. H. Feng, Y. Li, S. Lin, E. V. Van der Eycken and G. Song, *Susta. Chem. Proc.*, 2014, **2**, 14–19.
24. J. Spencer, R.P. Rathnam, H. Patel and N. Anjum, *Tetrahedron*, 2008, **64**, 10195–10200.
25. R. J. Rahaim and R. E. Maleczka, *Org. Lett.*, 2005, **7**, 5087–5090.
26. R. G. de Noronha, C. C. Romao and A. C. Fernandes, *J. Org. Chem.*, 2009, **74**, 6960–6964
27. C. Antonetti, M. Oubenali, A. M. R. Galletti, P. Serp and G. Vannucci, *Appl. Catal., A*, 2012, **421–422**, 99–107.
28. E. Kim, H. S. Jeong and B. Moon Kim, *Catal. Commun.*, 2012, **45**, 25–29.
29. R. Bendi and T. Imae, *RSC Adv.*, 2013, **3**, 16279–16282.
30. Y. Feng, A. Wang, H. Yin, X. Yan and L. Shen, *Chem. Eng. J.*, 2015, **262**, 427–435.
31. A. Wang, H. Yin, H. Lu, J. Xue, M. Ren and T. Jiang, *Langmuir*, 2009, **25**, 12736–12741.
32. A. Wang, H. Yin, M. Ren, H. Lu, J. Xue and T. Jiang, *New J. Chem.*, 2010, **34**, 708–713.
33. N. Mahata, O. S. G. P. Soares, I. Rodriguez-Ramos, M. F. R. Pereira, J. J. M. Orfao and J. L. Figueiredo, *Appl. Catal., A*, 2013, **464–465**, 28–34.
34. M. Tumma and R. Sriastava, *Catal. Commun.*, 2013, **37**, 64–68.
35. C. Rudolf, F. A. Ghaida, B. Dragoi, A. Ungureanu, A. Mehdi and E. Dumitriu, *Catal. Sci. Technol.*, 2015. DOI: 10.1039/C5CY00428D.
36. Y. Li, Q. Zhang, N. Zhang, L. Zhu, J. Zheng and B. H. Chen, *Int. J. Hyd. Ener.*, 2003, **38**, 13360–13367.

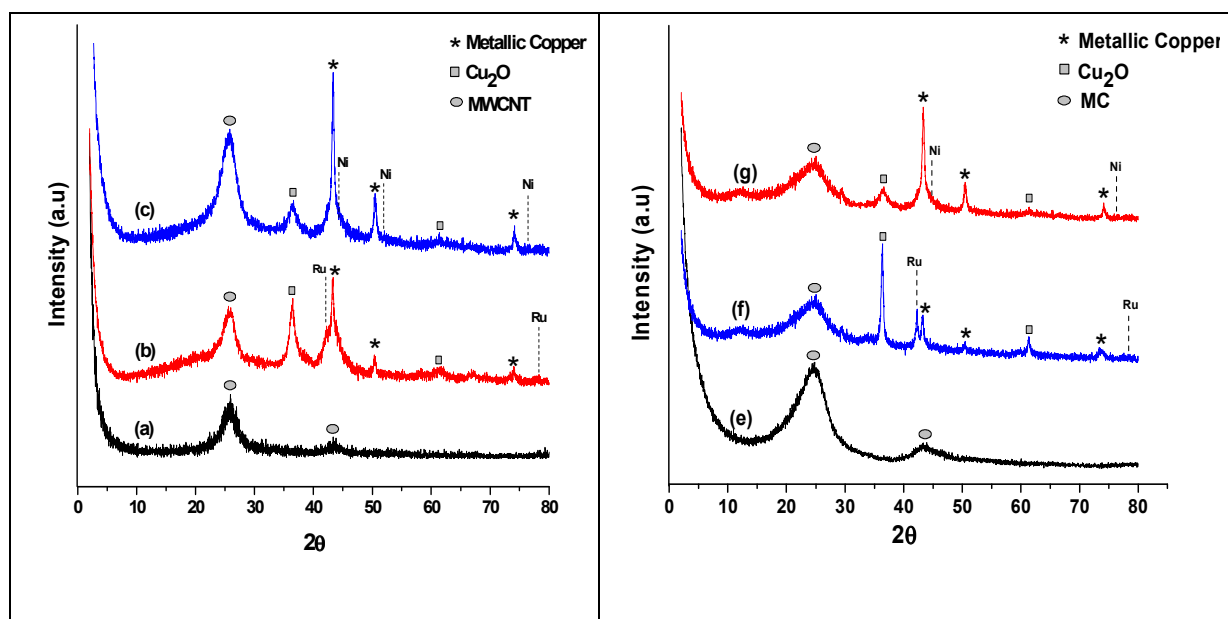
37. S. K. Singh, A. K. Singh, K. Aranishi and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 19638–19641.
38. L.M. Esteves, M. H. Brijaldo and F. B. Passos, *J. Mol. Catal. A: Chem.*, 2016, DOI:10.1016/j.molcata.2016.02.001.
39. P. P. Upare M. G. Jeong, Y. K. Hwang, D. H. Kim, Y. D. Kim, D. W. Hwang, U. H. Lee and J. S. Chang, *Appl. Catal., A*, 2013, **491**, 127–135.
40. S. G. Oh, V. Mishra, J. K. Cho, B. J. Kim, H. S. Kim, Y. W. Suh, H. Lee, H. S. Park and Y. J. Kim, *Catal. Commun.*, 2014, **43**, 79–83.
41. Z. Zhao, H. Yang and Y. Li, *RSC Adv.*, 2014, **4**, 22669–22677.
42. O. Mazaheri and R. J. Kalbasi, *RSC Adv.*, 2015, **4**, 34398–34414.
43. A. M. Tafesh and J. Weiguny, *Chem. Rev.*, 1996, **96**, 2035–2052.
44. X. Zhang, G. Wang, W. Zhang, Y. Wei and B. Fang, *Biosensors and Bioelectronics*, 2009, **24**, 3395–3398.
45. I. Stamatina, A. Moroza, A. Dumitru, V. Ciupina, G. Prodan, J. Niewolski and H. Figiel, *Physica E*, 2007, **37**, 44–48.
46. C. Li, J. Wang, Z. Jiang and P. Hu, *New J. Chem.*, 2015, **39**, 4562–4567.
47. P. Martis, A. Fonseca, Z. Mekhalif and J. Delhalle, *J Nanopart Res*, 2010, **12**, 439–448.
48. Z. Wu, Y. Mao, X. Wang and M. Zhang, *Green Chem.*, 2011, **13**, 1311–1316.
49. W. Zhen, B. Li, G. Lu and J. Ma, *RSC Adv.*, 2014, **4**, 16472–16479.
50. J. Chen, N. Xia, T. Zhou, S. Tan, F. Jiang and D. Yuan, *Int. J. Electrochem. Sci.*, 2009, **4**, 1063–1073.
51. C. P. Jimenez-Gomez, J. A. Cecilia, D. Duran-Martin, R. Moreno-Tost, J. Santamaria-Gonzalez, J. Merida-Robles, R. Mariscal and P. Maireles-Torres, *J. Catalysis*, 2016, **336**, 107–115
52. J. Fu, K. Yang, C. Ma, N. Zhang, H. Gai, J. Zheng and B. H. Chem, *Appl. Catal. B: Environm*, 2016, **184**, 216–222.
53. A. B. Dongil, B. Bachiller-Baeza, I. Rodriguez-Ramos, J. L. G. Fierro and N. Escalona, *RSC Adv.*, 2016, **6**, 26658–26667.
54. Y. Wang, Z. Rong, Y. Wang, P. Zhang, Y. Wang and J. Qu, *J. Catal.*, 2015, **329**, 95–106.
55. R. Chakravarti, A. Mano, H. Iwai, S. S. Aldeyab, R. P. Kumar, M. L. Kantam and A. Vinu, *Chem. Eur. J.* 2011, **17**, 6673–6682.



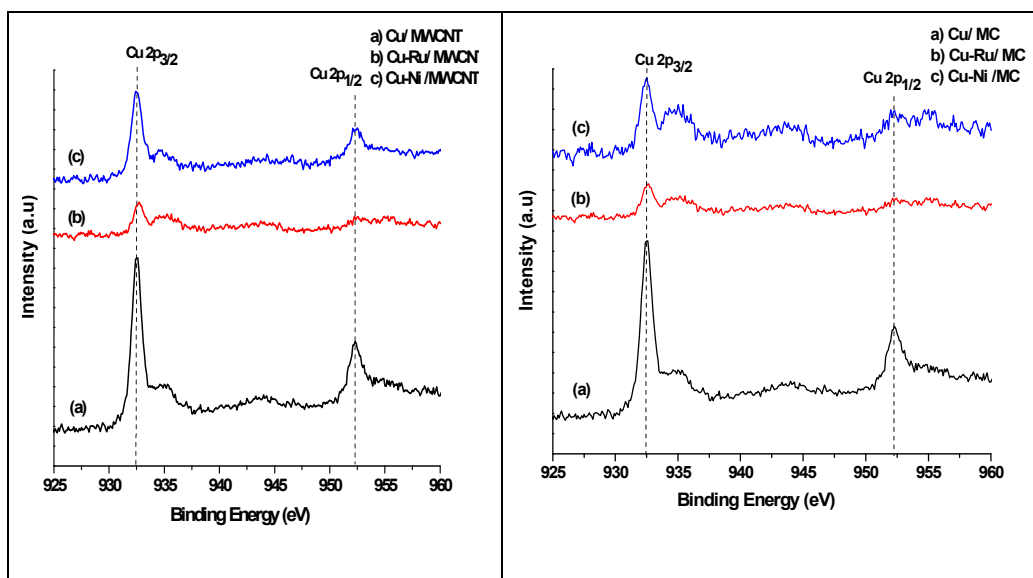
Figures: (1 to 3)



**Fig.1.** A plausible reaction mechanism for the reduction of 4-bromo nitrobenzene to 4-bromoaniline using Cu-Ru/MWCNT catalyst with NaBH<sub>4</sub> as hydrogen source.

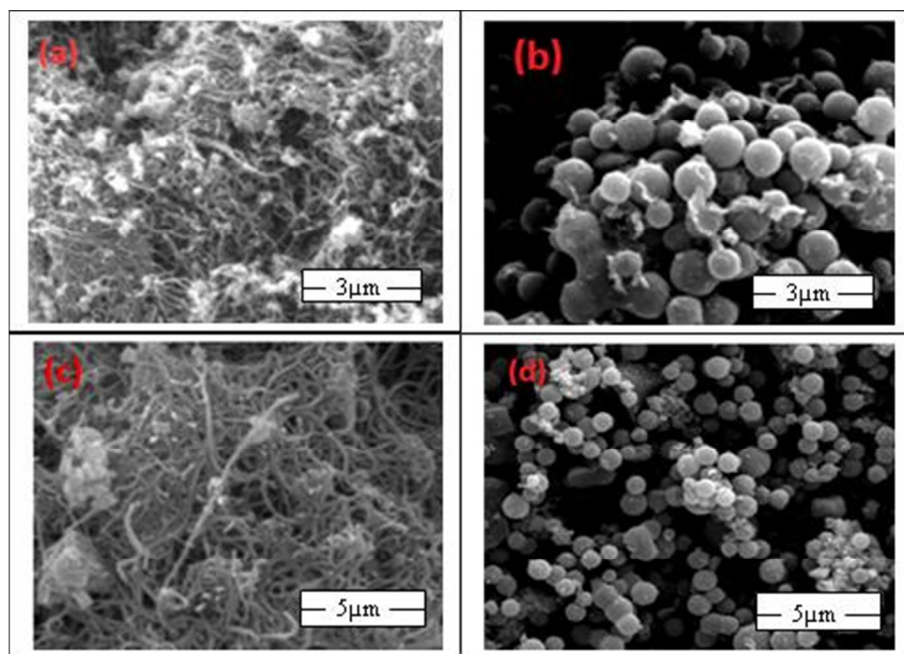


**Fig. 2.** Powder XRD Patterns of a) F/MWCNT, (b) Cu-Ru/MWCNT, (c) Cu-Ni/MWCNT, (e) F/MC, (f) Cu-Ru/MC and (g) Cu-Ni/MC catalysts.

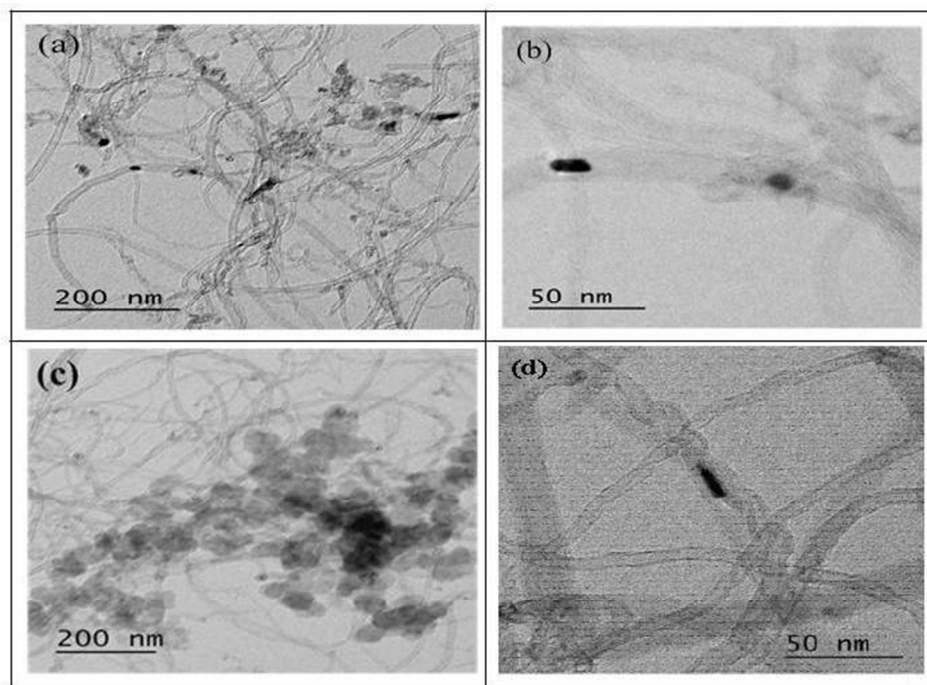


**Fig. 3.** XPS spectra of Cu, Cu-Ru and Cu-Ni supported on MWCNT and MC catalysts for copper 2p<sub>3/2</sub> and 2p<sub>1/2</sub> electrons.

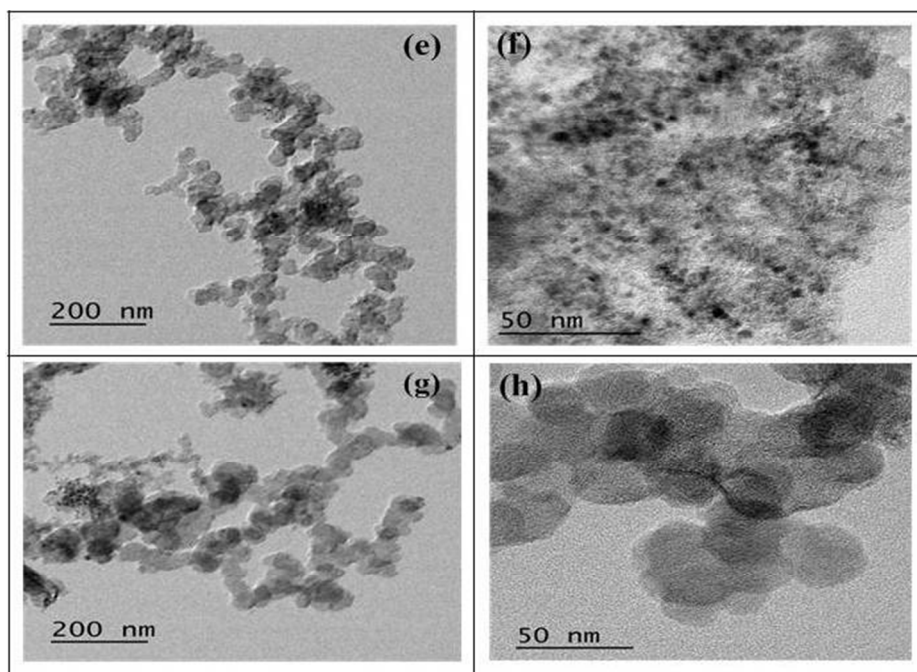
Figures: (4 to 6)



**Fig. 4.** SEM image of (a) Cu-Ru/MWCNT, (b) Cu-Ru/MC, (c) Cu-Ni/MWCNT and (d) Cu-Ni/MC catalysts.



**Fig. 5.** TEM image of (a, b) Cu-Ru/MWCNT and (c, d) Cu-Ni/MWCNT catalysts.



**Fig. 6.** TEM image of (e, f) Cu-Ru/MC and (g, h) Cu-Ni/MC catalysts.

## Graphical Abstract

