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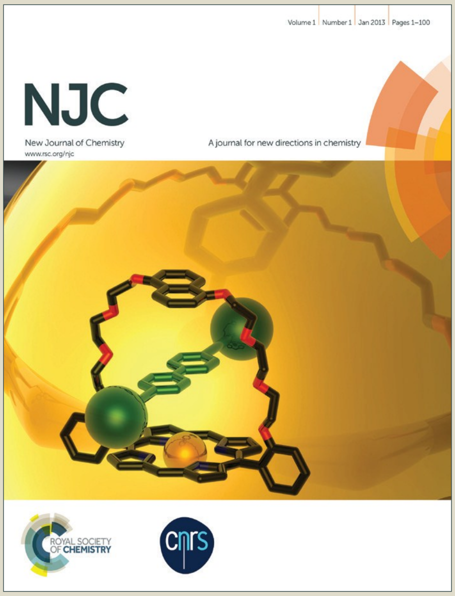

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$CoFe_2O_4$ Decorated Carbon Nanotubes for Dehydration of Glucose and Fructose

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Multi-walled carbon nanotubes (CNTs) decorated with different ferrites have been synthesized and successfully used under heterogeneous conditions in the dehydration of fructose. In addition inverse spinels like cobalt ferrite ($CoFe_2O_4$) , magnetite (Fe_3O_4) decorated on CNTs showed better performance than normal spinel like zinc ferrite ($ZnFe_2O_4$) decorated CNTs. The catalyst could be easily recycled and make the protocol simple. Moreover, functionalized CNTs were characterized by using various methods including Raman Spectroscopy, X-ray Diffreaction (XRD) and Transmission Electron Microscope (TEM) analysis. The crystallite size of $CoFe_2O_4$ decorated CNTs shows nearly 20 nm.

Industry favours a heterogeneous catalysis over homogeneous due to the advantage of recovery and recycling. Heterogeneous catalysis has been around for a long time, but has still much to groom. Due to their high thermal conductivity, high surface area, carbon nanotubes (CNTs) have evoked high interest not only for heterogeneous catalytic applications, but also in many important field such as fuel cell, lithium battery, composite materials and electric device.[1-3] While most of the CNTs can be used in various applications, there has been increasing demand for the functionalization of CNTs and consequently functionalized CNTs find a use in wide range of applications including catalysis.[4] In addition, CNTs distinguish themselves from other carbon materials such as activated carbon and carbon nanofibers because of well defined tubular structure formed by graphene layers.[5,6] CNTs decorated with magnetite nanoparticles are attractive particularly in heterogeneous catalysis due to ease of separation of the catalyst.[7] Surface functionalization of carbon materials with carboxyl group, amino group or hydroxyl group provides an efficient way of significantly improved performance of CNTs due to the enhanced compatibility and surface reactivity. All such functionalized groups of finds vital role in many catalytic reactions of homogeneous and heterogeneous type.[8] Besides, especially both carboxylic and sulfonic groups containing CNT groups finds applications extensively for phenol oxidation reactions [9a], and also in agar conversion, oxygen reduction reactions.[9b]

The hydroxymethylfurfural (HMF) which has been used in plastics, pharmaceuticals, and fine chemicals is mainly derived from petrochemicals at present, but it also could be obtained by the dehydration of various monosaccharides.[10] Recently, several remarkable catalytic systems have been explored, remarkably using acid catalysts in the dehydration of sacharadies.[11-12] In addition heterogeneous catalytic systems have also been developed for the dehydration of sugar moieties.[13-15] However, in most of the cases, along with HMF, other products like levulinic acid are also producing. Nevertheless, only a few catalytic systems have been realized to display only HMF as a sole product.

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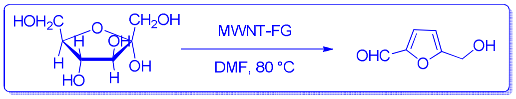
In the present communication, we are reporting the synthesis of HMF with high selectivity (up to 99%) using ferrite decorated CNTs form fructose (Scheme 1).



Scheme 1 Ferrite Decorated CNTs Catalyzed Dehydration of Fructose

Table 1 Ferrite-CNTs Catalyzed Dehydration of Fructose and Glucose

Entry	Catalyst	Reactant	Time(h)	Conversion (%)	Selectivity (%)
1	CNT	Fructose	24	N.R	-
2	CNT-COOH	Fructose	15	28	-
3	CNT-NH2	Fructose	15	32	-
4	Fe_3O_4	Fructose	6	10	-
5	Fe_3O_4	Glucose	10	N.R	-
6	$CoFe_2O_4$	Fructose	8	34	78
7	$CoFe_2O_4$	Glucose	12	N.R	-
8	$ZnFe_2O_4$	Fructose	24	N.R	-
9	CNT-Fe_3O_4	Fructose	6	22	98
10	CNT-$CoFe_2O_4$	Fructose	8	75, 74[a], 75[b]	99,98[a],99[b]
11	CNT-$CoFe_2O_4$	Glucose	10	64	98
12	CNT-$ZnFe_2O_4$	Fructose	8	N.R	-

Reactions were performed using 20.0 mg of catalyst, 180.0 mg of fructose, DMF: 3.0 mL at 80 °C. The reaction mixture was analyzed by using UV spectroscopy with Carrez solutions. [b]IInd cycle. [c]IIIrd cycle.

The multi walled CNTs and (**CNT**), amino functionalized CNTs (**CNT-NH$_2$**) were purchased from (diameter 12.9 nm and length 3-12 µm) from nanoshell laboratories, Haryana. The carboxylic acid functionalized CNTs (**CNT-COOH**), ferrite decorated CNTs were prepared according to the literature procedure.[16,17]

Initially, the unfunctionalized CNTs was employed as versatile heterogeneous catalyst for the dehydration of the fructose to HMF at 80 °C in DMF and the results are shown in the Table 1. The dehydration of fructose could not takes place with unfunctionalized CNTs (Table 1, Entry 1).[18] Very little conversion was observed with acid and base functionalized CNTs without HMF formation (Table 1, entrys 2& 3). Later the dehydration of fructose and glucose has been carried with different ferrites like Fe_3O_4, $CoFe_2O_4$ and $ZnFe_2O_4$ and the results are shown in the table 1 (entries 4-7). The inverse spinels like Fe_3O_4 and $CoFe_2O_4$ promotes the dehydration of fructose than normal spinel $ZnFe_2O_4$. Notably, less conversion of fructose using magnetite as a catalyst in the dehydration of fructose at 80 °C (10%) without HMF production whereas with $CoFe_2O_4$ 34% conversion with 78% selectivity of HMF was obtained. Of particular note is that no catalytic conversion of glucose was observed using Fe_3O_4 and $CoFe_2O_4$. Since ferrite decorated CNTs have been using as an attractive materials towards electro catalysis[19], adsorbents[20] and also as electrochemical sensor[21] are motivated to synthesize ferrite decorated CNTs. Therefore, CNTs were decorated with various ferrites which possess different magnetic properties like paramagnetic Fe_3O_4, diamagnetic $ZnFe_2O_4$ and electromagnetic $CoFe_2O_4$ were explored as recyclable catalysts in the dehydration of fructose (Table 1, entries 9 & 12). However, in the presence of magnetite-CNT, the rate of fructose dehydration increases significantly up to 22% conversion with 98% selectivity, Table 1, entry 9). Remarkably, neither $ZnFe_2O_4$ alone nor $ZnFe_2O_4$-CNT catalyzed the dehydration of fructose. (Table 1, entries 8 & 12). Substantial increase in catalytic power of $CoFe_2O_4$-CNT is highly remarkable in the dehydration of fructose up to 75% conversion with 99% selectivity to HMF. The low activity of $ZnFe_2O_4$ is attributed due to the diamagnetic property of the material and also may be electro negativity difference between the cobalt, iron and zinc. The higher activity of $CoFe_2O_4$-CNT and Fe_3O_4-CNT facile redox reaction Fe^{3+} to Fe^{2+} and Co^{2+} to Co^{3+} in an easier way because of the synergetic effect of CNT and ferrites and thus reaction proceeds in a smooth way. In the present study CNTs not only acts as a simple support but also promoting the reaction along with ferrites because of having extreme conducting properties. Moreover easy removal of the catalyst from the reaction mixture makes the procedure very simple for heterogeneous catalytic reactions (Table 1, entry 10). Although the rate of reaction is slow with glucose, however the selectivity towards HMF, up to 98% is highly remarkable (Table 1, entry 11). The significant increase in the activity of $CoFe_2O_4$ on CNT is due to its quite stability towards acidic and environmental conditions whereas Fe_3O_4 is quite reactive. The acidic hydroxyl groups of sugar molecule and also product HMF, might be having strong interaction with Fe_3O_4, which may lead to the reactivity in the dehydration reaction compared to $CoFe_2O_4$

The ferrite decorate CNTs were characterized by using Raman spectroscopy (Fig. 1). The Raman spectra exhibit the D and G bands typical of MWCNT. The two main typical graphite bands are present in the Raman Spectrum of MWCNTs bundles: the band at 1573 cm^{-1} (G band) assisted to the in-plane vibration of the C — C bond, typical of defective graphite-like materials and the band at 1343 cm^{-1} (D band) activated by the presence of disorder in carbon systems. The Raman spectrum also exhibits a band at 2677 cm^{-1} called the G’ band and attributed to the overtone of the D band. The ID/IG ratio of the Fe_3O_4, $CoFe_2O_4$ and $ZnFe_2O_4$ on CNT are 0.74, 0.81, 0.72 respectively. The orientation of the octahedral and tetrahedral sites of ferrites on CNTs might have caused the change in defective sites. In addition to that, some of the nanoparticles of ferrites can adopt the internal shape of the CNTs and accommodate them along the tube axis leading to enhancement of the magnetic anisotropy, which affects the increase the defective sites and hence the ratio. Further, the Raman spectra indicate that the radial breathing mode (RBM) of ferrite decorated CNTs below 500 cm^{-1} and broadened “G” line shows the presence of metallic character.[22]

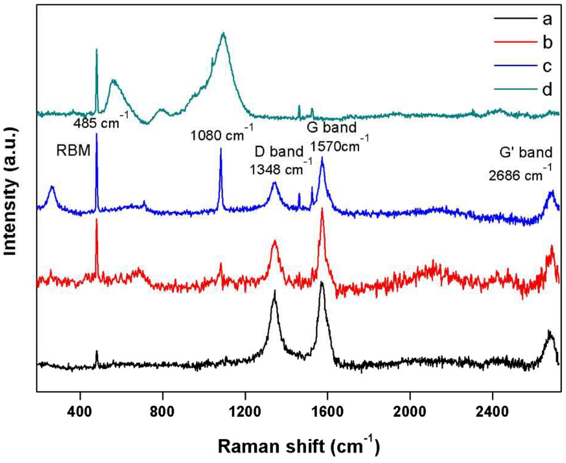


Fig.1. Raman Spectra of a) CNTs b) Fe_3O_4 on CNT c) $ZnFe_2O_4$ on CNT d) $CoFe_2O_4$ on CNT

In addition, the catalysts were also characterized by using X-ray diffraction (XRD). The crystallinity and structure of three spinels are confirmed by powder XRD. The peak position and relative intensity of all diffraction peaks for all the three samples are in close approximations with their respective reference pattern matched. In addition theta is equal to 26.2 indicates the presence of carbon nanotubes. The presence of (220), (311), (422), (511) revealed the cubic spinel phase of ferrites. The (002), (100), (101), (004), and (110) peaks are related to the presence of the CNTs. The (004) and (101) reflections are also due to flat graphitic layers, residual carbon particles, and the defect of the CNTs. The crystallite size was calculated using Scherer equation $D=0.89\lambda/B\cos\theta$ by taking maximum intensity peak FWHM for respective ferrites. It was found that average crystallite size of Fe_3O_4, $CoFe_2O_4$ and $ZnFe_2O_4$ is 16.4nm, 20.0 and 18.6 nm respectively (Fig. S3-S6). The magnetite has been conformed to mix phase in the crystal phase of cubic Fe_3O_4 along with Goethite (Fe_2O_3. H_2O) because of transformation of little magnetite to goethite under washing with CNTs, whereas cobalt ferrite exhibits cubic crystal structure.

Besides, the ferrite decorated CNTs were also characterized by using Scanning Electron Microscope (SEM) analysis. Agglomerations of metal oxide particles along the wall of CNT were observed (Fig. 2). The SEM images indicating-metal oxide particles (with some agglomerated state) set at open surface of lump MWCNTs which may be for catalysis applications.

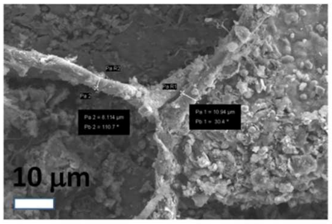


Fig.2. SEM of $CoFe_2O_4$ decorated CNT

Apart from other methods, the all the ferrites on CNTs were also characterized by TEM, which indicates the crystallite size is around 20 nm (Fig.2). The $CoFe_2O_4$, Fe_3O_4, $ZnFe_2O_4$ decorated CNTs are having the average diameter of 8.5 nm, 12 and 11.6 nm respectively.

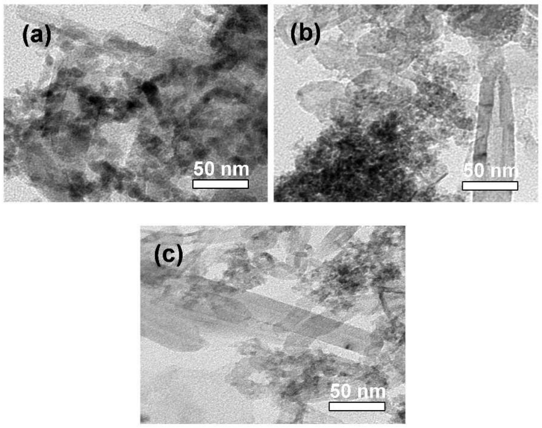


Fig.3. HR-TEM of (a) $CoFe_2O_4$ on (b) Fe_3O_4 (c) $ZnFe_2O_4$ on CNT

In conclusion, ferrite decorated CNTs have been successfully in the dehydration of sugar moieties. Moreover decoration of CNTs with ferrites acts as versatile heterogeneous catalysts with recyclability in the dehydration of fructose. Further work will try to understand the mechanism and possibility of asymmetric reactions will be of great interest.

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EXPERIMENTAL

To a suspension of functionalized CNT (20.0 mg) in DMF (3.0 mL) was added fructose (180.0 mg). The reaction mixture was heated to 80 °C with vigorous stirring. After completion of the reaction monitored by UV and HPLC (C-18 column, water:DMF/methanol 9.5:0.5:1, 1.0 mL/min flow rate), the reaction mixture was cooled to room temperature. The resulting solution was extracted several times with methyl butyl ether to get the pure product.

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$CoFe_2O_4$ Decorated Carbon Nanotubes for Dehydration of Glucose and Fructose

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Carbon nanotubes have been decorated with various ferrites of normal and inverse spinels were characterized by using XRD, Raman, SEM and TEM analysis. The inverse spinel decorated CNTs were successfully evaluated in the dehydration reactions.