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Journal Name

ARTICLE

Surface modification of ferrite nanoparticles with dicarboxylic acids for the synthesis of 5-hydroxymethylfurfural: A novel and green protocol

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The surface modification of nanomaterials is one of the rapidly growing research areas. Ferrite nanoparticles (inverse spinels) with average diameter of about 14 nms were modified with various structurally divergent dicarboxylic acids. Successful surface modification allows them to prevent the aggregation of nanoparticles. The modified materials showed good catalytic activity in the dehydration fructose to 5-hydroxymethylfurfural (HMF) under solvent free conditions first time. The HMF was synthesized in high yields under heterogeneous conditions. The flexible ligands modified ferrites showed good catalytic activity than rigid ligands modified ferrites.

Introduction

The catalytic activity of nanomaterials is dependent on the structure and composition of its surface. The surface properties can change in response to the variation of the environment because of these materials possess a unique property like high surface area and accessibility of various active facets.¹⁻⁴ The utilization of nanomaterials in various directions is increasing rapidly after surface modification (SM) due to change of their properties at the surface.⁵⁻⁷ Various methods have been employed for the SM, among which the silane, polymer and surfactant assisted methods are predominating.⁸ Carboxylic acids and amines were used as a versatile surface modifiers to significantly improve the performance of materials due to the enhanced surface reactivity.⁹⁻¹³ Particularly, mono carboxylic acids (long chain fatty acids) and primary amines are well known surface modifiers of TiO₂ and Palladium. Step wise SM of magnetite nanoparticles (MNPs) was carried out using aminopropylsilane, phosphonate group and alkyl substituted carboxylate.¹⁴⁻¹⁶ However, SM of MNPs with dicarboxylic acids have not been known for the catalytic applications. Although there are large number of SM materials, including metal oxides, but the true potential application of them is yet to be explored. Hence the development of highly active and surface modified catalysts for the synthesis of useful compounds has great importance.

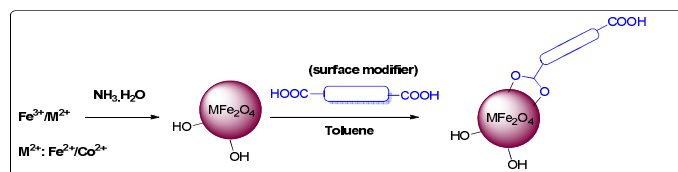
Development of new catalysts for the sustainability of green protocol is rapidly growing.¹⁷⁻¹⁹ Among the current biofuel sources, 5-hydroxymethylfurfural (5-HMF) converted from biomass is a versatile and key intermediate.²⁰⁻²²

Synthesis of 5-HMF has been realized by using homogeneous acid catalysed dehydration of mono and polysaccharides,²³ in the presence of water,²⁴⁻²⁷ isopropyl alcohol,²⁸⁻³¹ ionic liquid³² and also in biphasic system³³⁻³⁴. The direct acid catalysed dehydration of glucose to HMF, in water exhibits very low yields.³⁵⁻³⁹ Different metal halides in ionic liquids have been extensively studied as efficient dehydrating catalyst with moderate to good yields.⁴⁰⁻⁴² In the direction of heterogeneous catalysis, metal organic frame works⁴³, aluminium doped zirconium phosphate,⁴⁴ niobium catalysts⁴⁵ acts as a potential candidates for dehydration of sugar to 5-HMF. Well known metal oxides like sulphated zirconia,⁴⁶ sulfonic acid and ionic liquid functionalized silica,⁴⁷ mixed metal oxides,⁴⁸ ion exchange resins, amberlyst, metal phosphoric acids, functionalized CNTs and Mg-NHCs⁴⁹⁻⁵³ were used as heterogeneous catalysts for dehydration of sugar. However, one of the drawback is the selectivity towards 5-HMF is either low or it is having less reactivity or separation of the reaction mixture from catalyst is tedious.

In this context, herein we report the covalent SM of ferrites (inverse spinels) using various structurally divergent dicarboxylic acids and subsequent utilization in the HMF synthesis (Scheme 1).

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Scheme 1 Surface modification of ferrites with various dicarboxylic acids.

The inverse spinels selected for SM in our present case are superparamagnetic material MNPs (Fe_3O_4) and the electromagnetic material, cobalt ferrite (CoFe_2O_4). The surface of these two inverse spinels have been modified with various divergent dicarboxylic acids including oxalic acid (L1), succinic acid (L2), malic acid (L3) tartaric (L4) and terephthalic acids (L5) (Fig. 1). We chose them because of readily available and moreover dicarboxylic acids have not been used as surface modifiers for catalytic application to the best of our knowledge. Moreover, it is well known that acids catalyzed dehydration of sugar molecules.

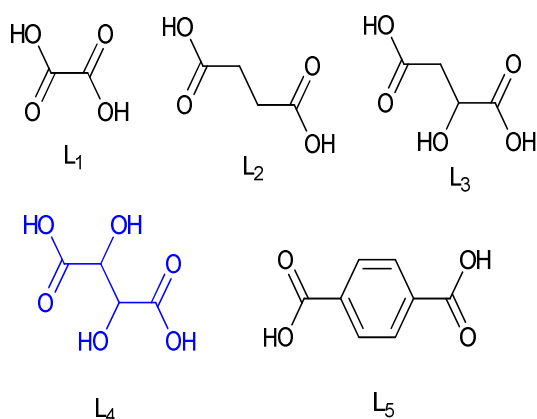
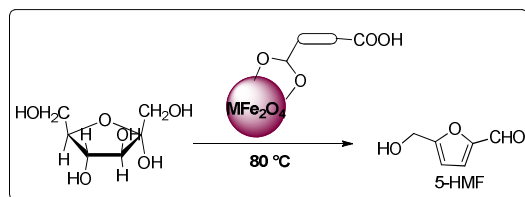


Fig. 1 Various flexible and rigid dicarboxylic acids used for surface modification of ferrites.

Surface modified ferrites provide the first example of an isolable and reusable heterogeneous catalyst in the dehydration of fructose under solvent free condition (Scheme 2). Solvent is required for separation of the HMF from reaction mixture. This work represents a novel method and is having more advantage towards environmental concern in the synthesis of HMF.



Scheme 2 Surface modified ferrites catalyzed the dehydration of fructose.

Experimental Section

Catalyst Characterization

All the reactions were performed in an oven-dried flask. All chemicals were purchased from Aldrich and used directly as received; Analysis of the reactions was done by HPLC from Shimadzu company with dual pump using C-18 column. Concentrations (c) are given in g/100 mL. Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (ν) of recorded IR-signals are quoted in cm^{-1} . Powder X-ray diffraction (XRD) measurements were performed using Bruker's D8 Discover X-ray diffractometer. It was equipped with Chromium target at source (radiation, $\lambda = 2.2897 \text{ \AA}$). The data was collected after minimizing the fluorescence correction of ferrite powders. All the data was collected over the 2-theta range of $20\text{--}120^\circ$ at a scan rate of 1.0° per second in diffraction patterns. The measured XRD data were evaluated using DIFFRAC, EVA, universal software supplied with Bruker's instrument. The correlation was done using PDF-2 release 2013, ICDD's for powder diffraction reference files. The diffraction patterns were compared with the supplied reference powder diffraction files (ICDD-PDF cards) for Fe_3O_4 and CoFe_2O_4 . Thus surface modified ferrite powders were matched with reference patterns of PDF 01-071-6336 for MNP and of PDF 00-028-1086 for cobalt iron oxides for phase identification. The SEM measurements were carried out using a field emission instrument (LEO 1530VP). Samples for SEM analysis were prepared on carbon coated copper grids; the instrument used was ZEISS Libra 200FE scanning electron microscope operated at 5 kV and equipped with a field emission gun, an in-column filter (Omega-filter), and a high-angle annular dark-field (HAADF) detector. All micrographs were taken with a 4K x 4K CCD camera and analysed with the software package Digital Micrographs (Version 1.71.38, Gatan Company). The EDX mapping was carried out with an EDAX elemental analyzed attached to the FE-SEM. A Tecnai FEI transmission electron microscope (TEM) operated at 200 kV accelerating voltage was utilized to evaluate the microstructure of the as prepared catalyst. X-ray photoelectron spectroscopic analysis (XPS) was performed using an ESCALAB250 instrument by Thermo VG Scientific. Unless stated otherwise, monochromatic $\text{Al K}\alpha$ -radiation was used (15kV, 150W, $\sim 500 \mu\text{m}$ spot diameter) with the transmission function of the analyzer having been calibrated using a standard copper sample; when necessary, charge compensation was achieved using a "Flood-Gun" ($\sim 6\text{eV}/0.05\text{mA}$). Spectra were recorded with pass energy of 80 eV for survey spectra, and 30 eV for core level spectra. For non magnetic samples, a magnetic lens was used to enhance the signal/noise ratio.

Synthesis of Ferrites

The MNPs were prepared by the so called wet-impregnation method as reported in literature.⁵⁴ The ultra-fine MNPs were prepared by co-precipitating aqueous solutions of ferrous ammonium sulphate $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and ferric chloride (FeCl_3) mixture, respectively, in alkaline medium. Ferrous

ammonium sulphate 0.98g (2.5 mmol) was added to 0.81 g (5 mmol) of ferric chloride in 200 mL of water (i.e., stoichiometry ratio $\text{Fe}^{2+}:\text{Fe}^{3+} = 1:2$) and the resultant mixture was kept at 80 °C for 30 min. To this solution, 0.02N NH_4OH was added drop by drop till the complete precipitation occurs under constant stirring. Magnetite formed by conversion of metal chloride into hydroxides (which takes place immediately), and hydroxides into ferrites. The resultant solution was maintained at 80°C for another 2h. Then the brown colour precipitate, obtained is washed several times with distilled water. The precipitate is then separated with the help of external magnet and is kept for drying at 80°C. Finally thus prepared MNPs were calcinated at 400°C for 2h to get free flowing powder.

Synthesis of cobalt ferrite nanoparticles

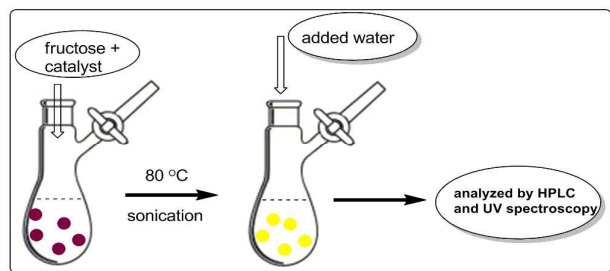
Cobalt ferrite nanoparticles were synthesized similar to that of MNPs, using cobalt chloride 0.59g (2.5 mmol) ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) instead of ferrous ammonium sulphate.

Surface modification of ferrites

The surfaces of ferrites were modified various dicarboxylic acids immediately after their synthesis. In an oven dried round bottomed flask, ferrite (1 mmol) was added to dicarboxylic acid (0.1 mmol) in dry toluene (5.0 mL). Later, the reaction mixture was stirred at 80 °C for 6 h and the surface modified ferrites were separated with the help of external magnet. Thus, obtained brown colour precipitation was finally washed with dry toluene (2 X 10.0 mL) and the resultant solid was dried at 80 °C for 5 h.

Synthesis of 5-HMF from fructose

In an oven dried flask, 180 mg of fructose and 30 mg of SM-ferrites were mixed and sonicated the mixture without solvent. The brown colour mixture was kept in at 80° C till yellow color appears. Later, 2.0 mL of HPLC water was added to the reaction mixture to separate the desire product. Later, the surface modified catalyst was recovered with the help of external magnet. The yellow aqueous reaction mixture was analysed by HPLC and UV-visible spectroscopy (Scheme 3).



Scheme 3. Schematic representation of HMF synthesis using surface modified ferrite nanoparticles.

A green and sustainable protocol developed, is used for the dehydration reaction, by adding the SM catalyst and fructose into a tube, without any solvent (Scheme 3).

Results and Discussion

The composition and phase purity of the as synthesized and SM catalysts were characterized by XRD using Chromium $\text{K}\alpha$ source. It was found that the intensity of diffraction peaks are consistent with the standard pattern. The sample shows very broad peaks, indicating the ultra fine nature and small crystallite of the particles. It is obviously seen that all the diffraction peaks can be indexed very well to MNPs (Fig. 2) and cobalt ferrites (Fig. 3). The obtained XRD pattern illustrated that, after modification, the characteristic peaks have been broadened, suggesting that dicarboxylic acids grafted on the lattice plane of MNPs and cobalt ferrite from all direction. The cubic single phase systems has been observed and size of the crystals were calculated using Debye-Scherrer formula. The crystallite size was found to be 13.5 nm and 8.5 nm, 9.7 and 7.7, 7.8 and 7.6 nm after the SM with ligands L1, L2 L3, L4 and L5 respectively. This may be due to the interaction of iron with modifier than Fe-Fe interactions and therefore prevents the agglomeration of MNPs. The phase identification and quantification is given in the table S1. The crystalline size of SM cobalt ferrite was found to be after the SM with ligands L1, L2 L3, L4 and L5 respectively 9.8 nm, 6.2, 6.7, 6.9 and 7.2 nm respectively (Fig. 3).

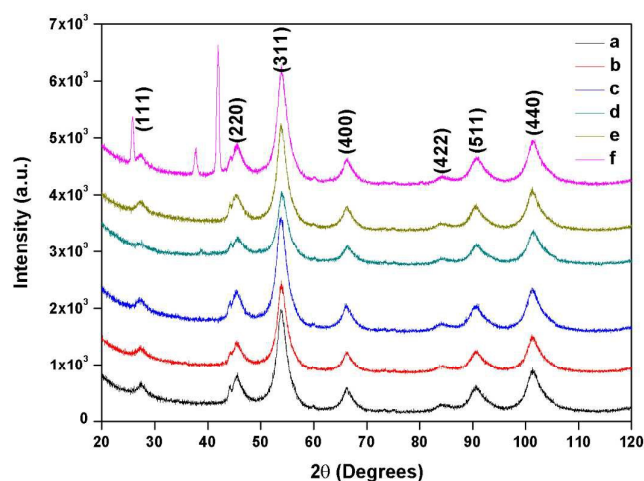


Fig. 2 XRD of (a) freshly prepared magnetite (b) surface modified with L1 (c) with L2 (d) with L3 (e) with L4 (f) with L5

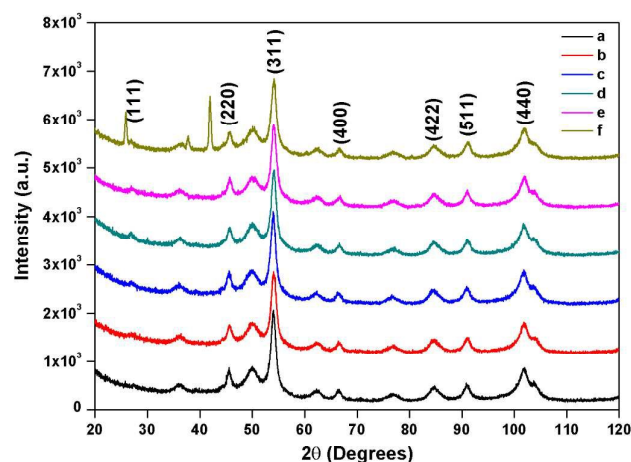


Fig. 3 XRD of (a) freshly prepared cobalt ferrite (b) surface modified with L1 (c) with L2 (d) with L3 (e) With L4 (f) with L5

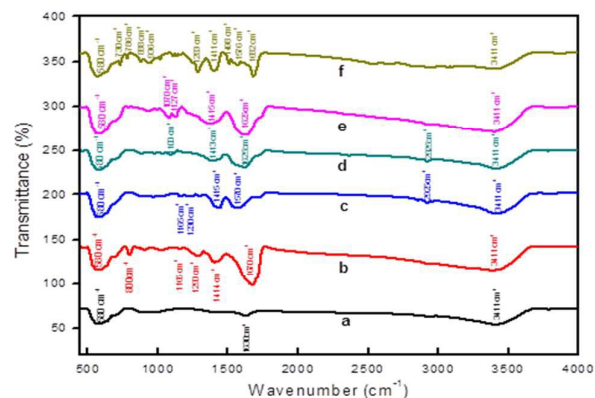


Fig. 4 FT-IR spectroscopy of (a) freshly prepared MNPs (b) surface modification with L1 (c) L2 (d) L3 (e) L4 and (f) L5

In addition, FT-IR spectroscopy revealed that surface of MNPs have been modified (Fig. 4). The Fe–O stretching vibration frequency at 580 cm^{-1} was observed for freshly prepared MNPs and also after SM. Notably, the stretching frequency at 1100 cm^{-1} is due to the presence of C–C bond of surface modifiers (Fig. 4, b-f). Moreover, the stretching frequency at 1415 cm^{-1} confirms the presence of carboxylate group. Of particular note is that C–H and C=C stretching vibration frequencies are observed at 786 cm^{-1} and 1576 cm^{-1} of aromatic group for L5 modified MNPs (Fig. 4, f). In addition the presence of –O–H stretching frequency in all the cases nearly 3400 cm^{-1} and deformed vibration of O–H is at 1630 cm^{-1} is (due to the coordinated surface –O–H groups with Fe-atoms) also present. These findings revealed that a significant SM of the ferrite nanoparticles. All stretching frequency assignments are given in the table S2. Similarly CoFe_2O_4 modified samples were also characterized by FT-IR and the results are included in the supporting information (Fig. S2). Further, the SM catalyst was characterized by using the scanning electron microscopy/energy-dispersive X-ray analysis (SEM-EDX). The morphology of the magnetite shows the presence of rod type structure and the surface is composed of well-aligned small nanoparticles for L1-L4 modified particles and stacked on each other for L5 modified ones (Fig. S3).

We commenced our study with the dehydration of fructose using L1 modified MNP as a catalyst system. We were pleased to find that running the reaction without solvent at 80°C , the fructose conversion was 18% with 84% selectivity for HMF. In order to better understand the role of surface modifier, the reaction was also carried out without SM. The conversion of fructose could take place only <5% either with Fe_3O_4 or CoFe_2O_4 (Table 1, entry 1 and 2). In order to understand the role of L1, various surface modified ferrites were prepared. Then, these modified ferrites were tested in the dehydration of fructose at 80°C . Remarkably when the surfaces of MNPs were modified with L3, and L5, fructose was dehydrated in 21% and <5% respectively (Table 1, entry 5 & 6). There was less selectivity towards HMF, although it shows good conversion (upto 86%) with L2 modified catalyst (Table 1, entry 4).

Table 1. Synthesis of 5-HMF using different surface modifiers.

Entry	catalyst	Time (h)	Conversion (%)	Selectivity (%)
1	Fe_3O_4	24	<5%	-
2	CoFe_2O_4	24	< 5%	-
3	Fe_3O_4 -L1	12	18	84
4	Fe_3O_4 -L2	12	86	<5%
5	Fe_3O_4 -L3	10	21	96.4
6	Fe_3O_4 -L4	3	98, 91 ^b	87, 83 ^b
7	Fe_3O_4 -L5	10	<5%	-
8	CoFe_2O_4 -L1	18	12	82
9	CoFe_2O_4 -L2	24	16	-
10	CoFe_2O_4 -L3	24	29	95
11	CoFe_2O_4 -L4	1	96	89
12	CoFe_2O_4 -L5	24	-	-

Reaction conditions: Catalyst: 30 mg, fructose: 180 mg at 80°C

This may be due to the flexible linear chain structure of L2 ligand, which forms bridging or chelating chemisorptions with MNPs (Fig. 5). Although conversion of fructose is less, selectivity towards HMF is high with malic acid, L3 modified MNPs. Notably, the yield of HMF drastically increased when the surface was modified with L4, *i.e.* with (*L*)-tartaric acid (Table 1, entry 6). This may be due to the availability of both hydroxyl and carboxylic acid groups which are responsible for higher catalytic activity.^{16,20} However, in the case of L2 and L5 the catalyst may not possess free COOH; hence either no selectivity or no catalytic activity was observed (Table 1, entry 7 and 12). This may be due to the binding orientation of the ferrites with surface modifiers (Fig. 5), which may not favour the formation of 5-HMF. It is reasonable to assume that L2, L3 and L4 (flexible ligands) forms chelating chemisorptions with MNPs. However, L5 forms the layers by layer structure, stacked one above the other (Fig. 6) as confirmed from SEM image (by interacting one ligand with two particles at the same time (Fig. 5, structures **ii** and **v**).

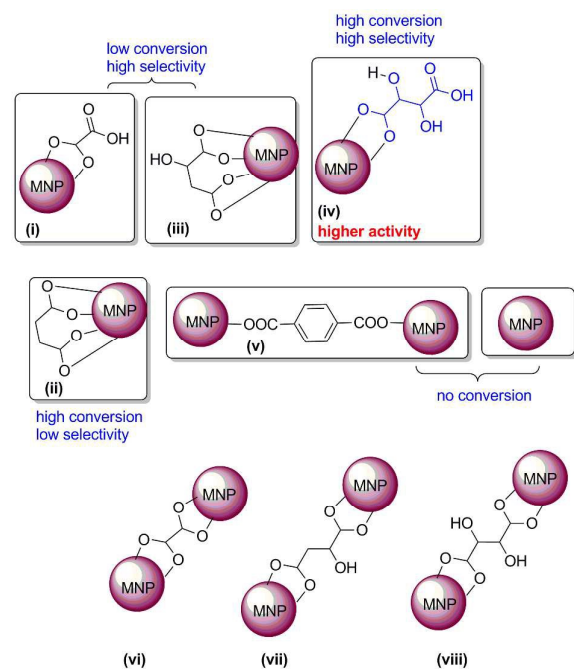


Fig. 5. Possible interaction of MNPs with various surface modifiers

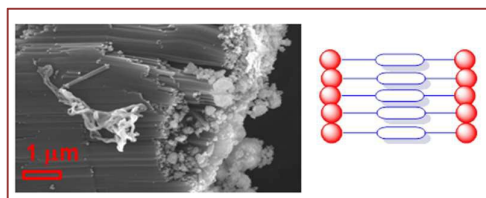
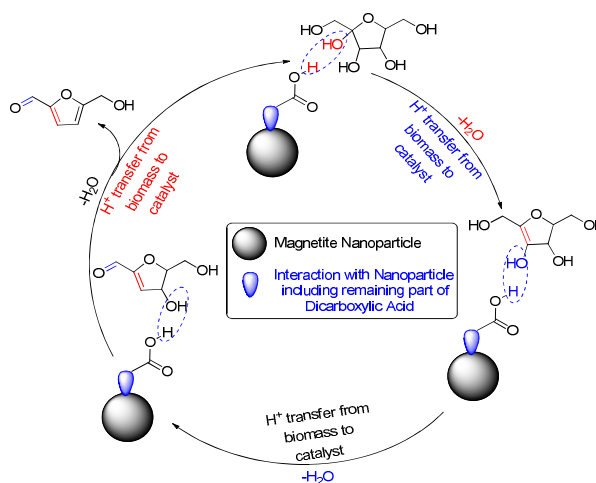


Fig. 6 SEM image of surface modification of MNPs with L5.

The major by products formed in the present case are over oxidized product, 2,5-furandicarboxylic acid and levulinic acid. Remarkably, the selectivity towards 2,5-furandicarboxylic acid is more when L2 modified ferrites were used in the dehydration reaction and moreover naked ferrites are known for oxidation of aldehydes and alcohols.⁵⁵ According to the observation that, both carboxylic acid and hydroxyl groups are accelerates the formation of HMF. We envision that the interaction of surface modifiers with ferrite is as shown in the fig 5.

From all these data we can ruled out the possibility of catalytic activity with the **vi**, **vii** & **viii** orientations of the Fig.5. If it happens, it could have showed less selectivity as like in the case of L2 modified MNP and almost no reactivity as like in the case of L5 modified MNP (Fig. 5). To the best of our knowledge, this is the first heterogeneous report for the synthesis of HMF under solvent free conditions (Table S3).

The mechanistic proposal of detailed dehydration of fructose to 5-HMF has been represented in the scheme 3. At first the acidic part of SM catalyst interacts with OH group of fructose and as a result one water molecule is removed from the moiety. The proton of the biomass transfers to catalyst and thereby SM catalyst regains its acidic property and active for removal of another water molecule. Finally 5-HMF is produced after removal of three moles of water (Scheme 3).



Scheme 3 Proposed mechanism for the dehydration of fructose using surface modified MNPs.

Catalyst recycling

In order to investigate the possibility of recycling the surface modified MNPs, the solid catalyst was separated from the reaction mixture by external magnet. The separated catalysts were washed several times with ethanol. The recyclability of SM-MNP was carried out by adding fresh fructose to the recovered catalyst. No efficiency loss was observed in dehydration to four successive runs under identical reaction condition (Fig. 7). In the case of cobalt ferrite nanoparticles, also ligand L4 exhibits higher catalytic activity of up to 96% conversion with 89% selectivity in one hour (Table 1, entry 8-12).

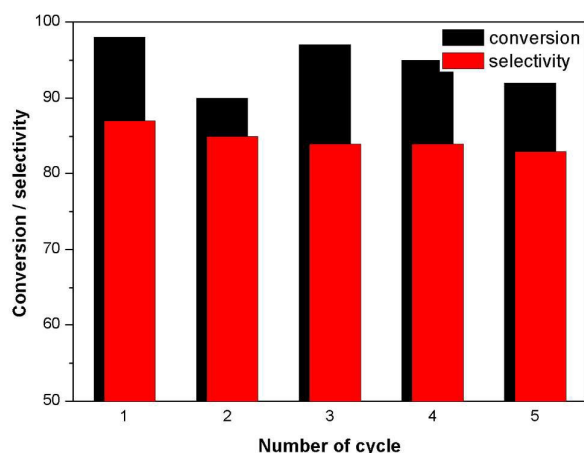


Fig. 7 Reusability of surface modified MNPs in the dehydration of fructose.

The SM catalyst was characterized by XPS before and after recycling. After recycling of the catalyst for five times, the binding energies for the Fe(II) and Fe(III) are not changed however, small increase in concentration of Fe(III) was observed (Fig. 8). Moreover, their SM by attachment with organic molecule stabilizes and prevents the oxidation of ferrites.

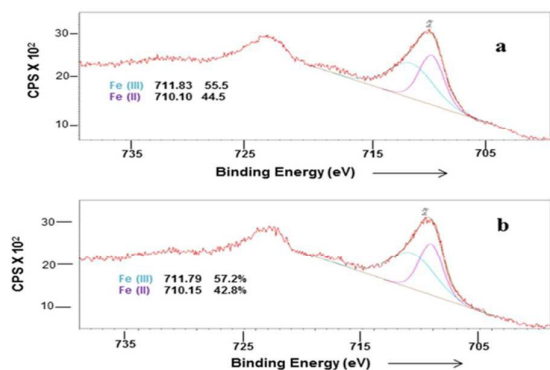


Fig. 8 XPS of the surface modified magnetite nanoparticle before and after recycling.

Additionally, the SM-MNPs were characterized by TEM. The TEM images of SM MNPs show that the average size of MNPs were in 11 nm in diameter and 18 nm after recyclability (Fig. 9).

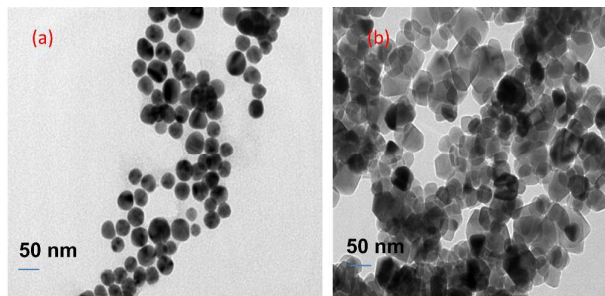


Fig. 9 HR-TEM of surface modified MNPs before and after catalytic reaction.

Conclusion

In summary, we have modified the surface of MNPs and CoFe_2O_4 NPs using dicarboxylic acids first time for the dehydration of fructose. The surface functional groups play a major role in the synthesis of HMF under solvent free conditions. The binding mode of ligand and orientation of surface modifier plays a major role in yields and selectivity. Easy removal of the catalysts after the reaction makes the procedure a very simple.

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