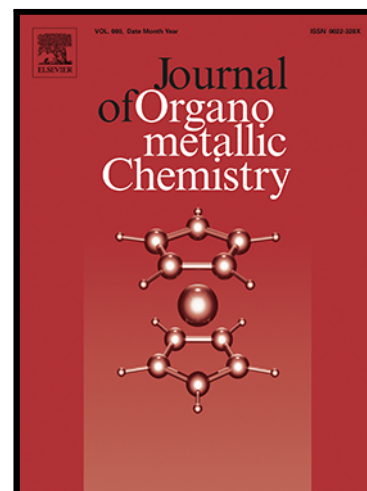# Journal Pre-proof

Acceptorless Dehydrogenative Oxidation of Primary Alcohols to Carboxylic Acids and Reduction of Nitroarenes via Hydrogen Borrowing Catalyzed by a Novel Nanomagnetic Silver Catalyst

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highlights

- Silver supported manganese ferrite nanoparticleswere synthesized and characterized.
- Acceptorless dehydrogenative oxidation and reduction of nitro arenes
- Recyclable by magnetic decantation in 5 consecutive cycles

Acceptorless Dehydrogenative Oxidation of Primary Alcohols to Carboxylic Acids and Reduction of Nitroarenes *via* Hydrogen Borrowing Catalyzed by a Novel Nanomagnetic Silver Catalyst

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This article is dedicated to the memory of Mohamad-Hadi Zolfaghari

Abstract

A novel silver nano magnetic catalyst was devised for dehydrogenative oxidation of aromatic and aliphatic alcohols to the corresponding acid with water as the sole oxygen source and hydrogen gas as the only by-product. The designed catalytic system advantages from easy recovery of magnetic materials *i.e.* magnetic decantation, being economically viable and environmentally friendly. Furthermore, the catalytic reaction is able to reduce aryl nitro compounds in the absence of any reducing agent.

1 Introduction

Oxidation reactions are one of the most important routes in synthetic organic chemistry.Traditional oxidants like potassium dichromate and permanganate focus on the addition of oxygen atoms accompanying the elimination of hydrogen as a water molecule. While oxidations employing these reagents are rapid and straightforward, the overall process results in generation of massive toxic waste, especially in industrial scale. Furthermore, catalytic hydrogen transfer oxidation, in which an organic acceptor is required, also suffers from this disadvantage. To overcome these problems, acceptorless dehydrogenative oxidation has been devised as an alternative protocol. During this process, hydrogen gas is liberated as the only by-product; which in addition to the elimination of any toxic waste, renders the whole catalytic process atom economical [1].

As most of oxidation reactions, oxidation of alcohols is classically performed by the use of stoichiometric amounts of toxic strong oxidants such as high-valent metal oxides and hyper-valent iodine. Even recently reported catalytic procedures involving cheap stoichiometric oxidizing agents like organic and inorganic peroxides or pressurized oxygen, suffer from inherent drawbacks, *e.g.* possible oxidation of organic solvents or other sensitive functional groups present in the starting material [2]. The glourious point in alcohol oxidation was acceptorless dehydrogenative oxidation which was pioneered by the Milstein group with the use of a homogeneous ruthenium catalyst [3]. Since then, various transition metal catalysts including Ru[4], Ir[5], Au[6], Ag[7], Pt[8], Cu[9], etc have been reported for this transformation for production of various target molecules.

Carboxylic acids with an application in a wide area of industries such as polymers, pharmaceuticals, solvents and food additives, constitute an important class of organic compounds. Industrial routes to carboxylic acids include oxidation reactions of various starting materials like hydrocarbons, aldehydes, alcohols and also carbonylation of alkenes [10]. Taking into account the importance of sustainability in industrial methodologies, the choice of alcohols is highly desirable, because a variety of alcohols are easily available from fermentation of biomass.

Acceptorless dehydrogenative oxidation of alcohols to corresponding carboxylic acids as an emerging synthetic strategy has received significant attention in recent years. Despite the progress in this era, the active metal cores of these catalysts focus on precious metals especially ruthenium, palladium and rhodium [11]. For instance, Milstein *et.al.* used a ruthenium pincer complex for acceptorless dehydrogentative oxidation of alcohols to carboxylic acids with water *i.e.* sodium hydroxide as the only oxygen source and hydrogen gas as the only byproduct [12]. Similarly, a synthetic

protocol based on catalysis activity of palladium on carbon was reported by Sawama group which took advantage of reduced pressure to shorten required time and temperature [13].

Nowadays in most of organic chemistry synthetic strategies there is a growing interest in the replacement of platinum group catalysts, with non-precious earth-abundant metals from the cost, availability and sustainability point of view [14]. Various remarkable characteristics of silver, such as its antimicrobial activity, being environmentally benign, besides its relatively low cost- as compared to gold, platinum, and palladium- makes it a feasible choice for dehydrogenative oxidation reactions. Despite the usefulness of silver for dehydrogenative oxidations, researches on this area are still scarce[13]. Nevertheless, the reported silver catalysts for acceptorless dehydrogenative oxidation of alcohols to carboxylic acids are associated with several problems, including difficulties in recycling of the catalyst [15].

Magnetic decantation of nanoparticles exhibiting superparamagnetic properties *e.g.* metal ferrites brings up an alternative strategy for catalyst recycling and removal from reaction mixture [16]. Hence, we decided to immobilize silver ion on the surface of manganese ferrite nanoparticles and study its catalytic application in dehydrogenative oxidation of alcohols to corresponding benzoic acids.

2 Experimental

2.1 Materials and Instrumentation

All chemicals and solvents were purchased from commercial suppliers and used without further purification. FT-IR spectra were obtained over the region 400–4000 cm−1 with a Nicolet IR100 FT-IR with spectroscopic grade KBr..XRD patterns were obtained at room temperature with a Philips X-pert 1710 diffractometer with Co Kα (λ = 1.78897 Å), 40 kV voltage, 40 mA current and in the range 10–90° (2θ) with a scan speed of 0.020° s−1. SEM (Philips XL 30 and S-4160) was used to study the catalyst morphology and size. Magnetic saturation of the catalyst was investigated using a vibrating magnetometer/alternating gradient force magnetometer (VSM/AGFM, MDK Co., Iran). TGA was conducted using a thermal analyzer with a heating rate of

20 °C min^{-1} over a temperature range of 25–1100 °C under flowing nitrogen. The hydrodynamic diameter of the nanoparticles was measured using a Zetasizer Nano MAL1001767 (Malvern Instruments, Malvern, UK) by DLS with the nanoparticles sonicated in water before the measurement. ^{1}H NMR spectra were recorded with a Bruker Avance (DRX 500 MHz, DRX 250 MHz) in pure deuterated dimethyl sulfoxide solvent with tetramethylsilane as internal standard.

2.2 Preparation of manganese ferrite (MnFe2O4) nanoparticles(MnFe)

Manganese ferrite nanoparticles were prepared according to a modfied previously reported literature[17]. To a solution containing 10 mmol $FeCl_3.6H_2O$(2.16 g) and 5 mmol $MnCl_2.4H_2O$(0.59 g) in 50 mL water, was added 20 mL 3 M solution of sodium hydroxide at 90 °C under vigorous stirring. After 1 hour, the resulting precipitate was collected by the aid of magnetic decantation, washed several times with water and ethanol and dried at 75°C for 24 hours. Next, nanoparticles were calcined at 900°C for 5 hours in an electrical furnace.

2.2 Immobilization of 3,3'-thiodipropanoic acid on the surface of manganese ferrite nanoparticles(MnFe-S)

1 g of as prepared manganese ferrite nanoparticles were dispersed in 50 mL methanol and 2 mmol of 3,3'-thiodipropanoic acid was added to the suspension and refluxed for 24 hours. Then the nanoparticles were collected using an external magnet, washed consecutively with water and ethanol and dried overnight at 50 °C.

2.3 Impregnation of 3,3'-thiodipropanoic acid-functionalized manganese ferrite nanoparticles with silver ion(MnFe-S-Ag)

To 1 g of nanoparticles prepared in the previous section(MnFe-S) which was dispersed in 50 mL methanol, 1 mmol of silver nitrate and 0.5 mmol NaOH was added and the mixture was stirred at room temperature for 24 hours. The resulting nanoparticles were subsequently washed with water and ethanol and dried overnight at 50 °C.

## 2.4 General procedure for dehydrogenative oxidation of alcohols

1 mmol of alcohol, 2 mmol (112 mg) potassium hydroxide and 30 mg of prepared catalyst (MnFe-S-Ag) were mixed in a reaction flask and 2 mL mesitylene was also added. The mixture was stirred for 24 hours at 160°C under argon atmosphere. The reaction progress was monitored using TLC analysis. When the reaction was considered complete, the catalyst was collected with a permanent magnet. Then solvent was evaporated under reduced pressure. Water (10 mL) was added to the resulting mixture to dissolve salts. The starting material was removed to the organic layer, with extraction of the reaction mixture with EtOAc (3×10 mL). Subsequently, the aqueous layer was acidified to pH 5-6 with a 20% HCl solution (2-5 mL). The target acid was generated as a white to yellow precipitate. Then it was extracted to EtOAc (3×10 mL) and the crude product was obtained after evaporation of the organic solvent and it was further purified by recrystallization if necessary.

2.5 General procedure for reduction of nitroarenes via hydrogen borrowing

To a mixture of 1 mmol of the nitro-aromatic compound and 1.5 mmol of benzyl alcohol (162 mg) in 2 mL mesitylene, was added 3 mmol (168 mg) of potassium hydroxide and stirred at 160°C for 24 hours. When the reaction was considered complete, using TLC, the catalyst was magnetically removed from the reaction mixture. After that, the solvent was removed using a rotary evaporator. Then water was added to dissolve inorganic salts, as well as benzoate ion. Next, the amine product was extracted to EtOAc (3×10 mL). The organic phase was washed with a slightly acidic aqueous solution (HCl 1M). The aqueous layer was separated using a separatory funnel and the target amine was liberated from the aryl ammonium moiety by subsequent addition of sodium hydrogen carbonate. To obtain the pure amine, the resulting mixture was extracted with EtOAc(3×10 mL), dried over Na_2SO_4 and the solvent was removed *in vacuo.*

3 Result and discussion

The schematic pathway for preparation of MnFe-S-Ag is illustrated in Scheme 1. Each precursor in every step and the final nanoparticles were investigated by the means of Fourier Transform Infrared (FT-IR) spectroscopy (Figure 1). The observed bands at 486 cm^{-1} and 608 cm^{-1} can be attributed to the stretching vibrations of Mn-O and Fe-O bonds which are intrinsic to core $MnFe_2O_4$ which is in good aggrement with reported ones [17]. C-O stretching vibrations of the ligand appeared at 1386 cm^{-1}. The carbonyl functional group of the ligand was observed at 1543 cm^{-1} in the MnFe-S-Ag nanoparticles. The aliphatic hydrogens of the ligand appeared at about 2900 cm^{-1}. The broad absorption band at 3300-3400 cm^{-1} is ascribed to surface OH groups of the manganese ferrite nanoparticles.
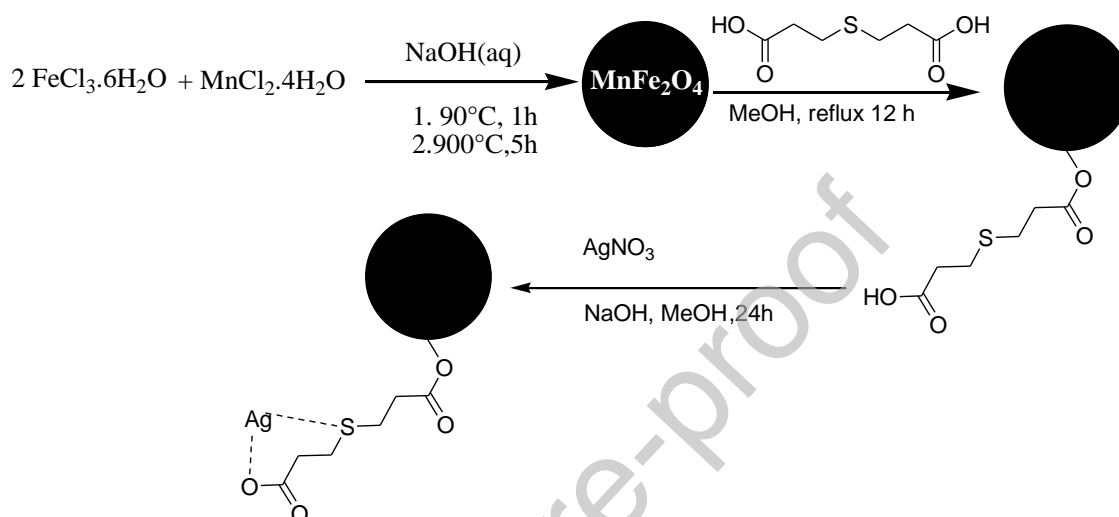
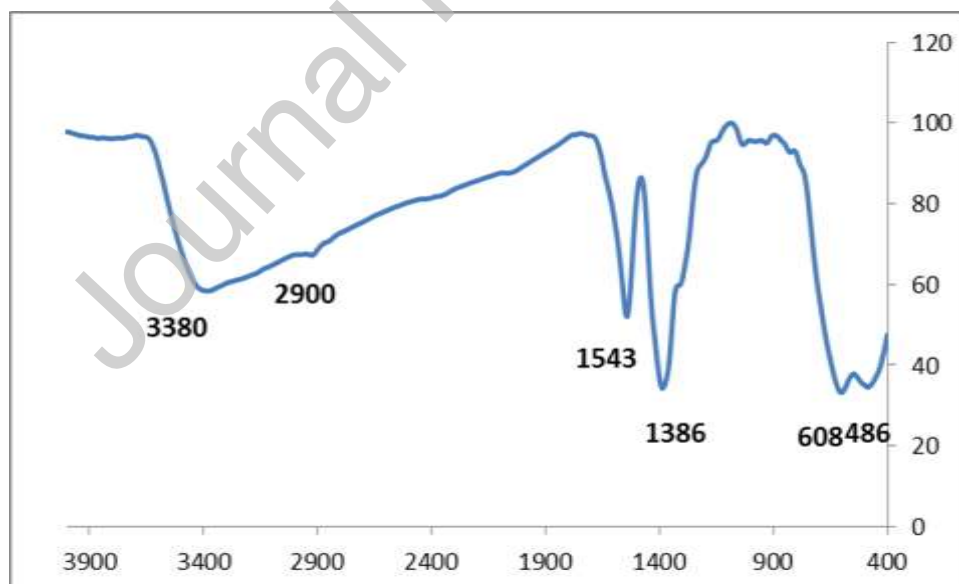**Scheme 1.** Pathway to the synthesis of MnFe-S-Ag nanoparticles

Fig. 1 FT-IR spectrum of MnFe-S-Ag nanoparticles

X-ray diffraction (XRD) pattern (Figure 2) was applied to prove the formation and stability of the manganese ferrite core of the synthesized nanoparticles. Seven diffraction peaks appeared at 2θ= 21.13, 34.85, 41.21, 50.30, 62.42, 66.43 and 73.68

which are characteristic peaks of pure $MnFe_2O_4$ according to JCPDS card no.74-2403[18].
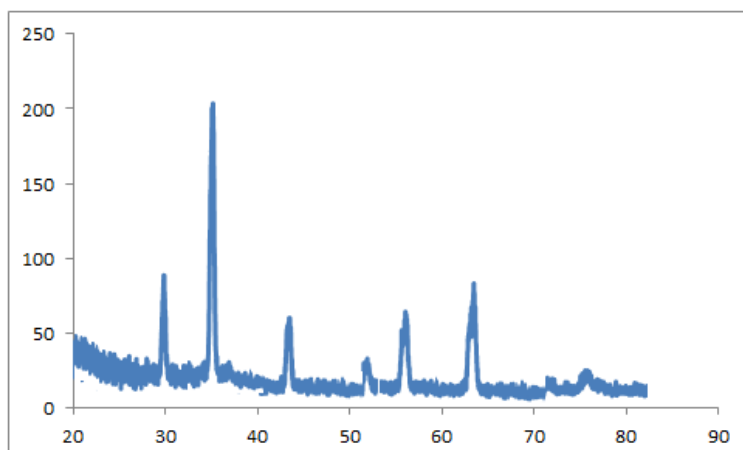

Fig. 2 XRD pattern of MnFe-S-Ag nanoparticles

Hysteresis loop of the prepared nanoparticles is depicted in Figure 3. The figure is the result of measurement of the magnetic properties of the sample using vibrating sample magnetometry in an applied magnetic field sweeping from -1000 to +1000 Oe. The magnetic saturation of the MnFe-S-Ag is about 50 emu g^{-1} at room temperature which is very high to facilitate easy magnetic separation from a liquid mixture[19]. Furthermore, zero remanence of the loop indicates the superparamagnetic properties of the nanoparticles.
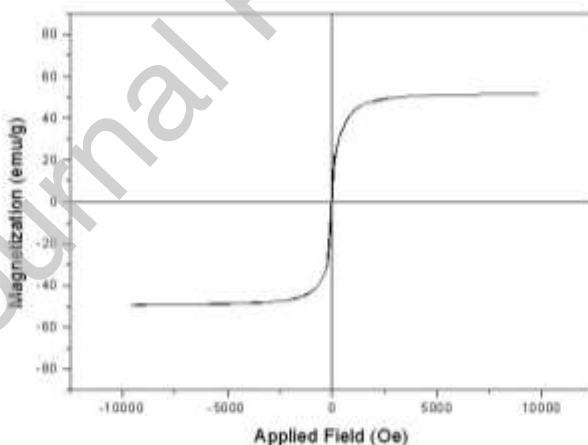

Fig. 3 Vibrating sample magnetometry of MnFe-S-Ag nanoparticles

Thermogravimetric analysis was performed for the quantitative determination of organic moieties anchored to the surface of magnetic nanoparticles (Figure 4). The weight loss below 200 °C is due to the loss of adsorbed surface water (8%). The second rupture in the diagram between 200-600°C is attributed to the elimination of attached organic groups which is about 11%.
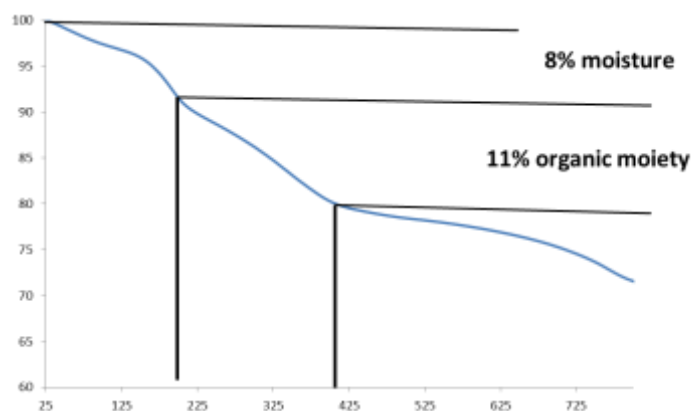
Fig. 4 Thermogravimetric analysis of MnFe-S-Ag nanoparticles

The morphology of MnFe-S-Ag nanoparticles was determined using scanning electron microscopy (SEM). The SEM image (Figure 5) confirms the uniform and nanoparticle sized sample. The particles are almost spherical in shape with the size range of 16-22 nm.
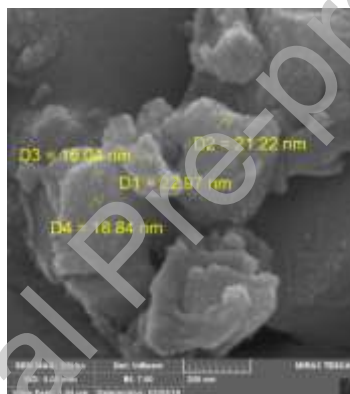

Fig. 5 SEM image of MnFe-S-Ag nanoparticles

Chemical composition of the prepared nanoparticles was studied using energy-dispersive x-ray spectroscopy (EDX). The resultant diagram (Figure 6) ensures the presence of constitutional elements of the magnetic core (Mn, Fe), ligand (C, O, S) and the coordinated metal ion (Ag). This strictly confirms the successful synthesis of the target nanoparticles.
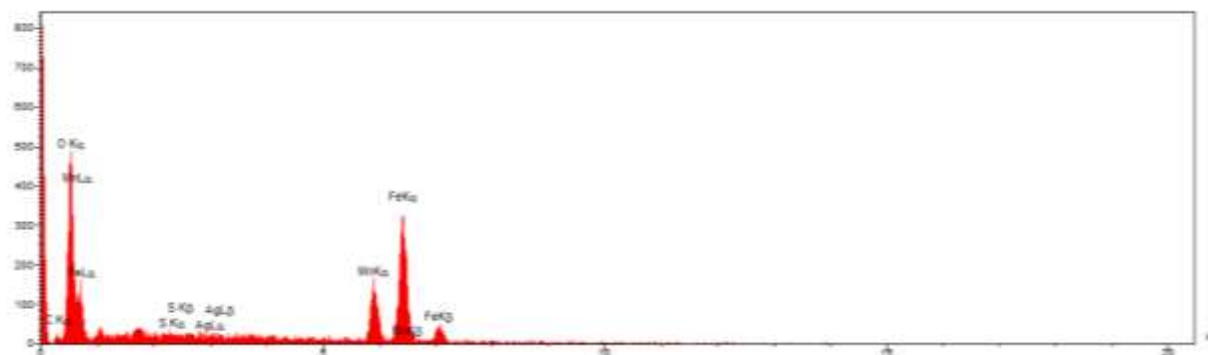
Fig. 6 EDS analysis of MnFe-S-Ag nanoparticles

The precise amount of constituent metallic elements of MnFe-S-Ag nanoparticles was determined by means of ICP analysis (Table 1). The ratio of Fe/Mn is 2.1 which is near to ideal stoichiometric formula. Furthermore the actual amount of iron and manganese in the prepared nanoparticles is less than the starting amount of their metal precursors(10 and 5 mmol respectively) which implies a negligible inefficiency in coprecipitation method.

Table 1. ICP analysis of metallic elements of MnFe-S-Ag nanoparticles [a]

Entry	Metal element	amount(mmol/g)
1	Fe	9.85
2	Mn	4.69
3	Ag	0.032

The catalytic activity of prepared nanoparticles was tested in the dehydrogenative oxidation of alcohols to the corresponding acid. First of all oxidation of benzyl alcohol was opted as the model reaction (Scheme 2). Different reaction conditions were tested (Table 2). We discovered that reaction in DMF resulted in 70% of product. The reaction also proceeds in Ethanol, acetonitrile, toluene and water but lower yields. Using mesitylene as the reaction solvent and potassium hydroxide as the base resulted in the best yield of all.

KOH(2eq),cat(30 mg)(0.096 mol%)
solvent,reflux,24h, Ar
2.HCl(aq) work up
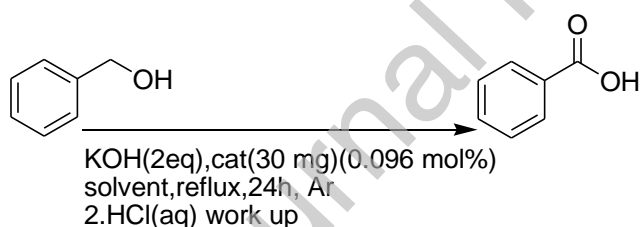
Scheme 2. Oxidation of benzyl alcohol

Table 2. Optimization of reaction conditions of benzyl alcohol oxidation [a]

Entry	Catalyst(mg)	Solvent	Yield [b](%)
1	30	H_2O	38
2	30	CH_3CN	20
3	30	EtOH	23
4	30	DMSO	65
5	30	DMF	70
6	30	Toluene	40

| 7	30	Mesitylene	90
8	-	Mesitylene	-
9	30[c]	Mesitylene	-
10	60	Mesitylene	92

a Reaction conditions: benzyl alcohol(1 mmol), KOH(2 mmol), solvent(1 mL),reflux.

b Isolated yield.

c Fe_3O_4 nanoparticles.

Having optimized reaction conditions in hand, we explored the substrate scope of the reaction (Table 3). Conversion of double bond in cinnamyl alcohol to 3-phenylpropanoic acid proves the liberation of hydrogen gas. Moreover, it was observed that halogen substituents were removed when the reaction was conducted for 24 hours. Thus for these derivatives, we studied the reaction in a much shorter period. In this instance, no dehalogenation occurred. Moreover, the effect of electron-withdrawing substrates was surveyed using 3-NO_2-benzyl alcohol. Separation and characterization of the product proved a complete reduction of the nitro group to its corresponding amino counterpart [20]. This attempted us to test the reaction for reduction of different nitro compounds (Table 4).

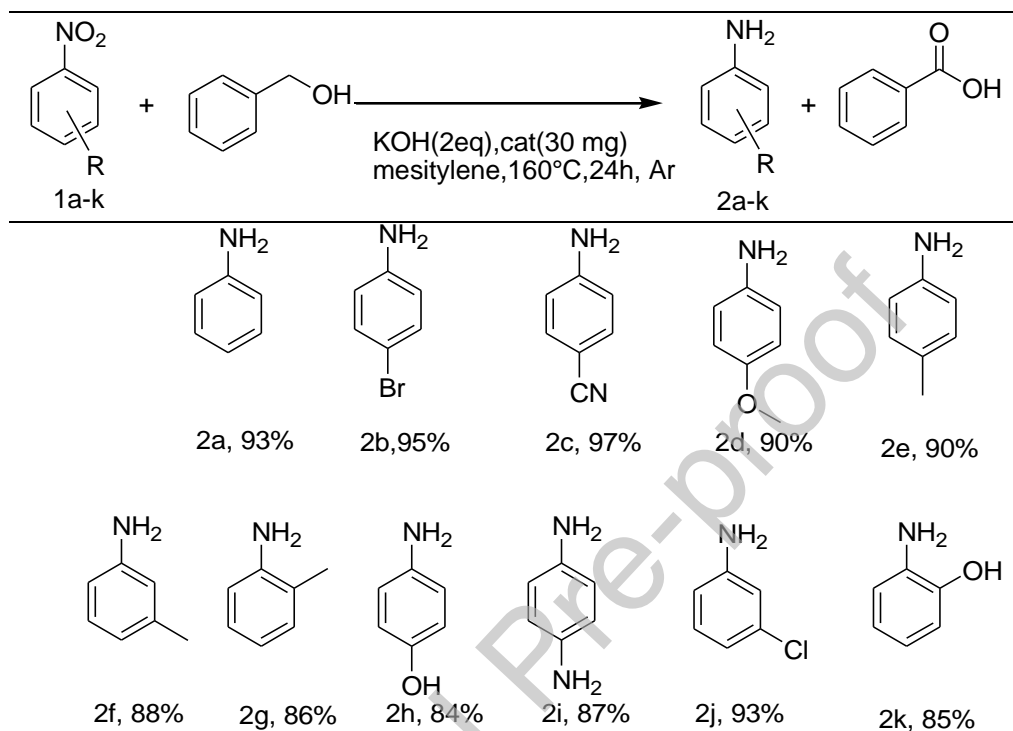**Table 3.** MnFe-S-Ag catalyzed oxidation of benzyl alcohol.
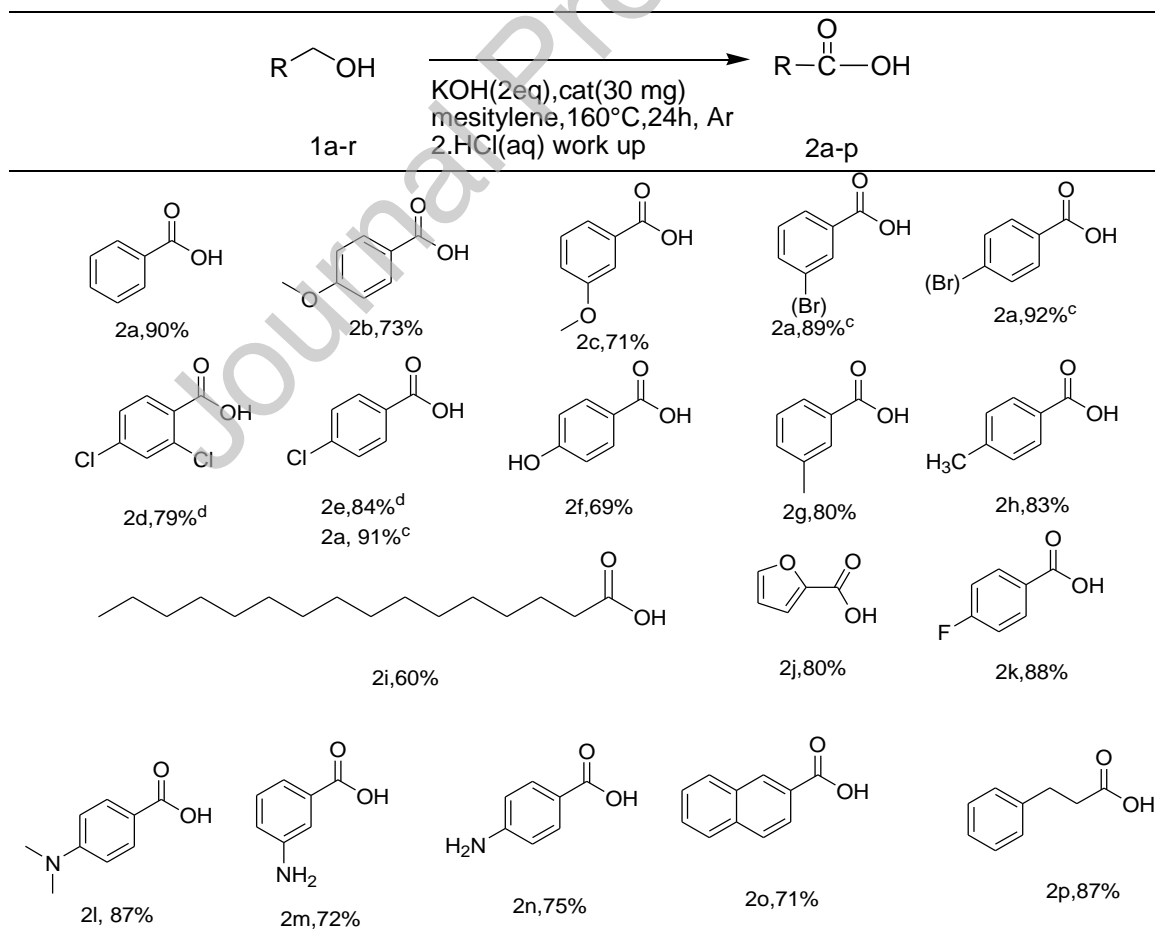
a Reaction conditions: benzyl alcohol(1 mmol), KOH(2 mmol), catalyst(30 mg) Mesitylene(1 mL),160°C .

b Isolated yield.

c Substituted starting material, unsubstituted product(benzoic acid)

d Shorter reaction time (3 hours)

Table 4. MnFe-S-Ag catalyzed the reduction of nitroarenes.

a Reaction conditions: benzyl alcohol(1.5 mmol), nitro arene (1 mmol), KOH(2 mmol), catalyst(30 mg) Mesitylene(1 mL),160°C .

b Isolated yield.

In both of the reactions, the starting materials bearing electron donating substituents, the product obtained in relatively lower yields. It is apparent that steric hindrance also affected the reaction in a moderate manner. Moreover, aliphatic substrates reacted much more slower than the aromatics.

Finally, catalyst recyclability was tested using the model reaction. After completion of the reaction, the catalyst was separated with the aid of magnetic decantation and washed with ethanol, water and diethyl ether in consequence. The reaction vessel was charged with starting materials and the process was repeated for 4 times until observation of a noticeable drop in catalytic performance. The results are depicted in Figure 7. It is apparent that after each test, a negligible reduction in product yield occured. A considerable loss in product yield was observed after 6 [th] cycle. Besides, the heterogenetic nature of the catalyst was analyzed with simultaneous application of hot filtration test and ICP analysis which both confirmed the proposition *i.e.* the model reaction was conducted at optimized reaction conditions then the catalyst was removed from the reaction mixture after 4 hours and the reaction vessel bearing all the ingredients except the catalyst was stirred at the mentioned condition for another 24 hours. No promotion in reaction progress was observed. Furthermore ICP verification of

heterogeneity of the catalyst was conducted through water extraction of any possibly present silver ion after removal of catalyst and the product. To ensure any leached silver from the catalyst as silver element, the residual reaction mixture was treated with concentrated nitric acid to oxidize silver to silver ion so that complete extraction of silver to aqueous phase is occurred.
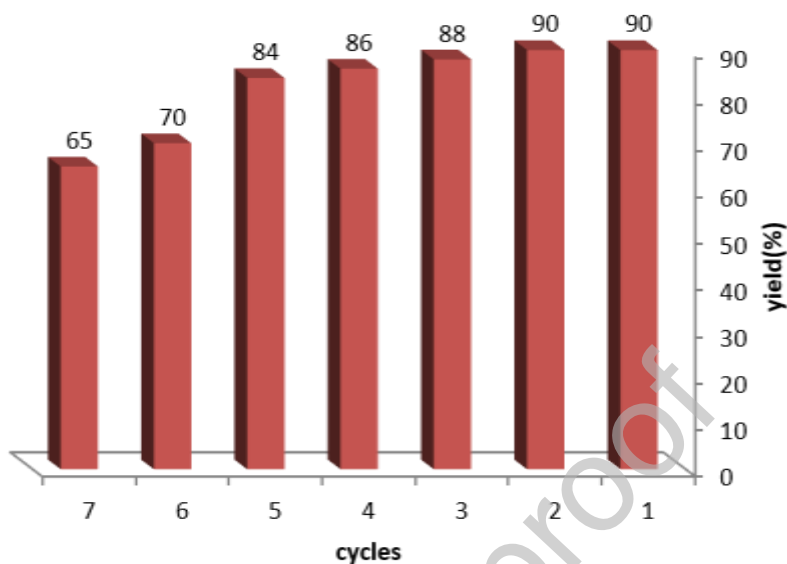

Fig. 7 Recycling of MnFe-S-Ag in the oxidation of benzyl alcohol

The Recycled catalyst was characterized after 5 [th] run and it showed no significant changes in its structure (Fig. 8).
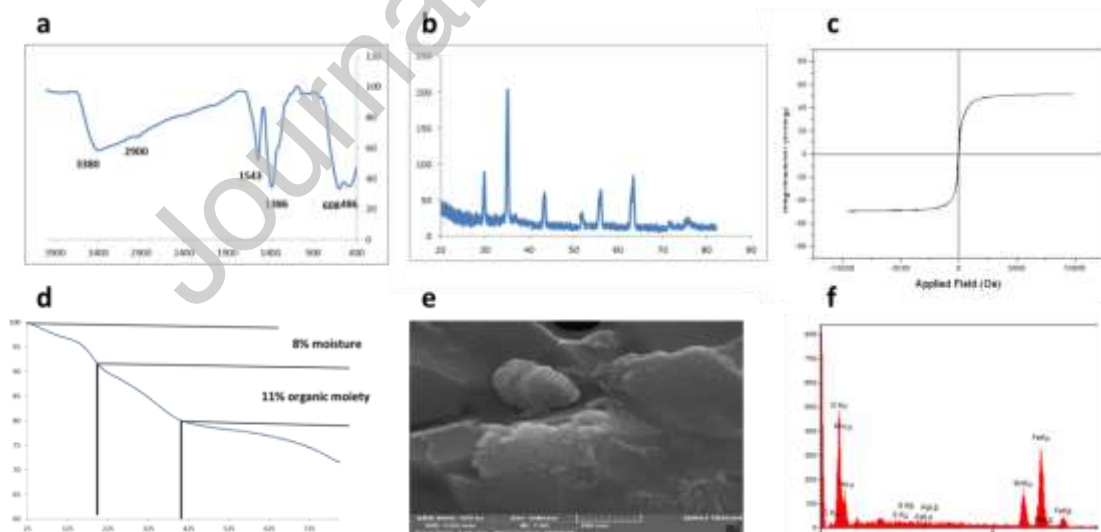

Fig. 8. a) FT-IR, b) XRD, c) VSM, d) TGA, e) SEM and f) EDS of recycled catalyst (after 5 [th] run)

A comparison between common Ag salts and prepared nanocatalyst was carried out in the oxidation reaction under the optimized reaction conditions. The results are reported

in table 5. It is apparent that prepared nanocatalyst is far more active in the oxidation of benzyl alcohol.

Table 5. Activity of different Ag sources in oxidation of benzyl alcohol [a]

Entry	Ag source(0.1 mol%)	Yield(%)
1	$AgNO_3$	45
2	$AgCl$	30
3	Ag_2CO_3	75
4	MnFe-S-Ag	90

A suggested mechanism can be observed in scheme 3. Initially, the alcohol is absorbed on the surface of nanoparticles(A) and then the proton of hydroxyl group is abstracted by the support(B). In the next step, carbonyl compound is formed during cleavage of the C-H bond of alkoxide by silver atom(C). Then silver hydride reacts with the abstracted proton to release hydrogen gas and the rendered catalytic surface which is ready for the next cycle [21].
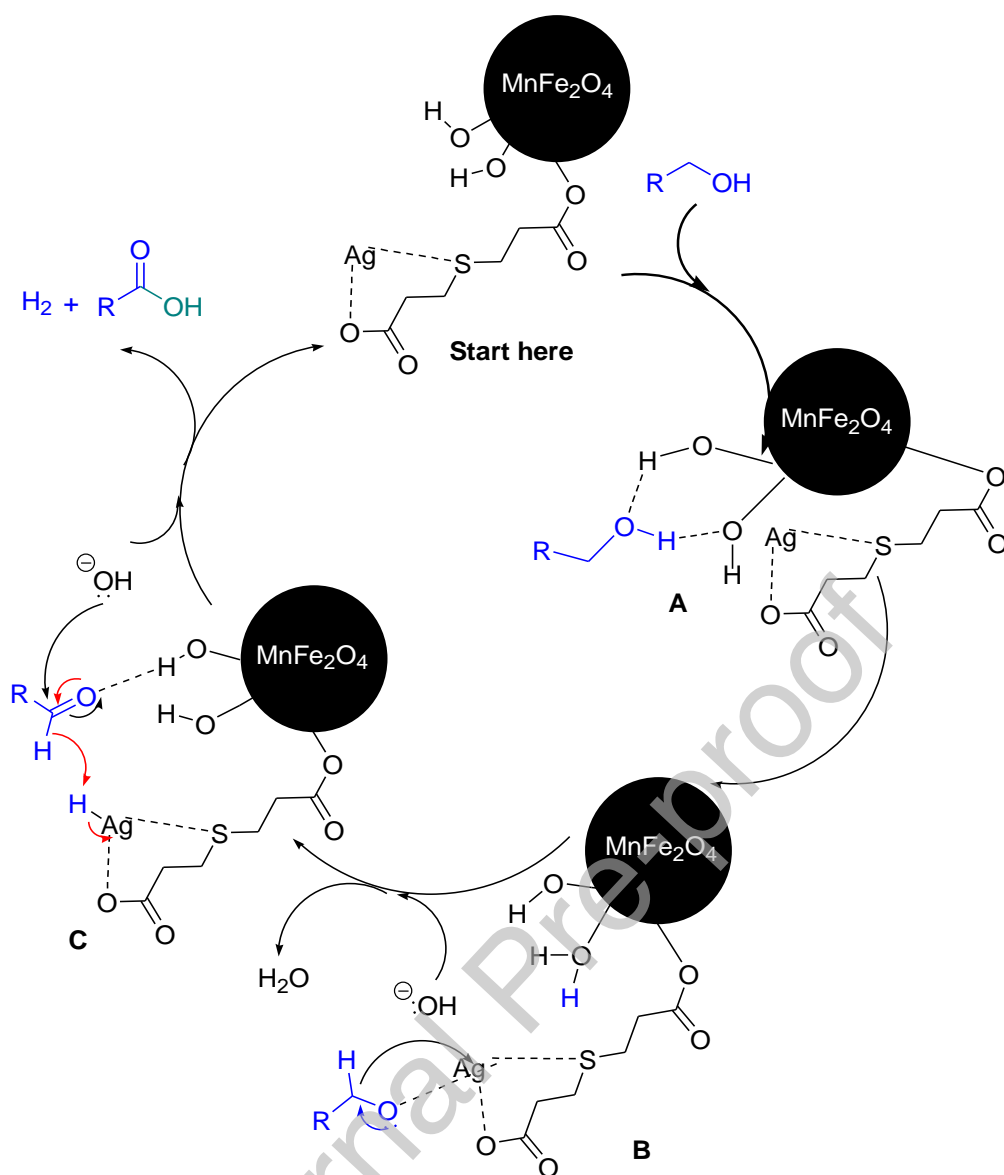
Scheme 3. Proposed mechanism for dehydrogenative oxidation of alcohols

4 Conclusions

In this research project, we prepared silver-impregnated manganese ferrite nanoparticles with its acceptable activity for dehydrogenative oxidation of alcohols and hydrogen borrowing strategy for the reduction of nitroarenes in moderate to good yields. This system was the first magnetic catalyst in this era which advantages the ease of separation and recyclability for 5 consecutive cycles. Furthermore this is the first heterogenous silver catalyst for acceptorless dehydrogenative oxidation of alcohols to carboxylic acids.

Supporting information

Spectroscopic and characterization data of catalyst and products are inserted in electronic supporting information file.

Compliance with Ethical Standards

Conflict of interest We declare that no conflict of interest exists.

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