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### Introduction

The selective oxidation of alcohols to their corresponding carbonyl compounds is one of the most useful reactions in industrial processes.1 Oxidation reactions are usually difficult and typically require stoichiometric amounts of toxic heavymetal salts or expensive catalysts involving noble metals, such as gold, ruthenium, rhodium, or palladium.<sup>2-5</sup> Traditionally, non-catalytic methods with stoichiometric, toxic, corrosive, and expensive oxidants, such as permanganate, dichromate, and peroxy acids, under stringent conditions of high pressure and/ or temperature have been widely used for alcohol oxidation.6-9 These reactions are also often carried out with high concentrations of bases and environmentally unfriendly organic solvents. Therefore, much attention has been paid to the development of heterogeneous catalytic systems that use clean and atom-efficient oxidants like molecular oxygen or H<sub>2</sub>O<sub>2</sub> without organic solvents.<sup>10-13</sup> Among these systems, the solventfree aerobic oxidation of alcohols using molecular oxygen or air as the oxidant has become more attractive,14-16 due to positive effects in terms of cost, safety, and environmental impact. In

## Nanoparticle-supported and magnetically recoverable organic-inorganic hybrid copper(II) nanocatalyst: a selective and sustainable oxidation protocol with a high turnover number<sup>+</sup>

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A magnetically recoverable copper-based nanocatalyst was prepared from inexpensive starting materials. With a particle size between 20 to 30 nm, it was shown to catalyze the oxidation of benzylic alcohols. The catalyst exhibited a high turnover number (TON) and excellent selectivity. The catalyst was characterized by several techniques, such as XRD, HR-TEM, SAED, EDS, FT-IR, VSM, and BET surface area. Factors affecting the reaction parameters, such as the substrate to oxidant molar ratio, weight of the catalyst, reaction time, *etc.*, were investigated in detail. The reusability of the catalyst was examined by conducting repeat experiments with the same catalyst; it was observed that the catalyst displayed no significant changes in its activity even after seven cycles for the aerobic, as well as for the peroxide, oxidation of benzyl alcohol. Furthermore, the heterogeneous nature, easy recovery, and reusability, makes the present protocol highly beneficial for addressing environmental concerns and industrial requirements.

this study, the objective was to develop an efficient catalytic system for the aerobic or  $H_2O_2$  oxidation of various alcohols under solvent-free conditions.

The copper-catalyzed oxidation of organic compounds has attracted significant attention in recent years,<sup>17</sup> owing to the high demand for mild and efficient oxidation catalysts.<sup>18</sup> Copper is an abundant metal in the Earth's crust and its redox properties make it ideally suited for catalytic oxidation processes, provided that the electron-transfer processes can be controlled by an appropriate ligand set. Therefore, a number of copper-catalyzed aerobic oxidation systems have been wellestablished.<sup>19</sup> They employ copper salts in combination with 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO),<sup>20</sup> and various N ligands such as 2,2'-bipyridine (Bpy),<sup>20c,h</sup> 1,4-diazabicyclo[2.2.2] octane (DABCO),<sup>20g</sup> and 4,4'-trimethylene-dipyridine (TMDP).<sup>20f</sup> However, they are homogeneous<sup>20</sup> in nature and an additional base is often needed,<sup>20c,d,h</sup> which limits their application in the oxidation of the base sensitive alcohols.

Over the last few years, magnetic nanoparticles (*e.g.*  $Fe_3O_4$ ) have been extensively investigated as inorganic supports for the synthesis of organic–inorganic hybrid materials. They are potential alternatives to conventional materials, being robust, readily available, high-surface-area heterogeneous catalyst supports.<sup>21</sup> They offer an added advantage of being magnetically separable, thereby, eliminating the requirement for catalyst filtration after completion of the reaction. Most importantly, when magnetic nanoparticles are used as supports, the size of the support materials decreases to the nanometer scale, and all

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of the catalytic sites on the external surface of the particles are accessible to the substrates.<sup>22</sup>

Hence, modified magnetic nanoparticles have received a lot of attention as a support for the incorporation of different transition metal ions.<sup>23</sup> However, most of these techniques require several reaction steps to introduce functional groups to the magnetic surface and often involve the use of organosilica precursors as an organic shell to prepare a suitable support for trapping the metal ions.<sup>24</sup> The latter are not only very expensive and toxic, but also involve complicated synthesis methods. Therefore, from both an environmental and economic point of view, the preparation of modified magnetic nanoparticles via a simple method and without using organoalkoxysilane compounds is highly desirable. In addition, although Fe<sub>3</sub>O<sub>4</sub>containing high performance catalysts for the oxidation of alcohols are reported,<sup>25</sup> the application of copper metal catalysts based on modified magnetic nanoparticles as heterogeneous catalysts in the oxidation of alcohols is not reported.

In continuation of our efforts toward the development of efficient nanoparticle-assisted catalysis,<sup>26</sup> herein, an Fe<sub>3</sub>O<sub>4</sub>–L-3,4-dihydroxyphenylalanine (LD) nanocomposite containing Cu<sup>2+</sup> ions (Fe<sub>3</sub>O<sub>4</sub>–LD–Cu) was prepared *via* a simple method as a novel heterogeneous magnetic catalyst. The main goal of this catalytic synthesis was to introduce a novel and efficient readily available copper as an effective catalyst, based on organic molecule-grafted magnetic nanoparticles to expand the use of these types of nanocomposites for catalytic oxidation reactions. A literature survey reveals that this type of catalytic system is less reported<sup>27</sup> for the aerobic and H<sub>2</sub>O<sub>2</sub> oxidation of alcohols. Initially, we used benzyl alcohol as the model system, to simplify the analysis and to accelerate the screening speed. Consequently, the optimized conditions were used for the synthesis of various aromatic aldehydes.

### **Results and discussions**

#### Catalyst characterization

We used magnetite nanoparticles ( $Fe_3O_4$ ), which were prepared by the co-precipitation method.<sup>28</sup> These were reacted with L-3,4dihydroxyphenylalanine (LD) in water to yield the  $Fe_3O_4$ -LD, and these obtained nanoparticles were further metallated with copper nitrate in ethanol to achieve the final copper complex grafted magnetically recoverable nanoparticles ( $Fe_3O_4$ -LD-Cu) (Scheme 1).

The High-Resolution Transmission Electron Microscopy (HR-TEM) images of the Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst shows a somewhat spherical morphology, with some cubic partials, and an average size range of 20-30 nm (Fig. 1A). Fig. 1B and C are the HR-TEM images of typical Fe3O4-LD-Cu at different magnifications. The nanoparticles, depicted in Fig. 1C and D, have a discrete core-shell structure, and a uniform magnetic core with a diameter of 10-15 nm surrounded by a 2-3 nm thick LD organic shell. The high resolution images in Fig. 1E show well developed lattice fringes, with the fringes extending throughout the particle, confirming the monocrystalline nature of the individual particles. The distance between adjacent lattice fringes was measured as 0.233 nm in Fig. 1E and corresponds to the 311 reflection. The selected area electron diffraction (SAED) pattern shown in Fig. 1F corresponds to the higher order reflections of the Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst. The white spots, as well as the bright diffraction rings, indicate that the nanoparticles produced by the above-stated method are highly crystalline.

The crystalline structures of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>–LD, and Fe<sub>3</sub>O<sub>4</sub>–LD–Cu were analysed by powder X-ray diffraction (XRD). As displayed in Fig. 2A to C, all the samples show diffraction peaks at around 30.1°, 35.2°, 43.1°, 53.5°, 57.4°, and 62.7° 2 $\theta$ , corresponding to the spinel structure of Fe<sub>3</sub>O<sub>4</sub>,<sup>29</sup> and which can be assigned to the diffractions of the (220), (311), (400), (422), (511), and (440) faces of the crystals, respectively. The relative intensities of the diffraction peaks matched well with the standard XRD data of the Joint Committee on Powder Diffraction Standards (JCPDS) card number (19-0629) for Fe<sub>3</sub>O<sub>4</sub> crystal with a spinel structure, which is consistent with the TEM results. In addition, the XRD patterns depict similar diffraction peaks, which indicate that the nanocomposite was synthesized without damaging the crystal structure of the Fe<sub>3</sub>O<sub>4</sub> core. In addition, the broad diffraction peak in the range of 2 $\theta$  between 10° and



Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst

Scheme 1 Schematic representation of the synthesis of Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst.



Fig. 1 HR-TEM images of magnetic  $Fe_3O_4$ -LD-Cu nanocatalyst at different magnifications (A) 50 nm, (B) 20 nm, (C) 10 nm, and (D) 2 nm, showing the particle size distribution. The resolved lattice fringes and SAED pattern of  $Fe_3O_4$ -LD-Cu are (E) and (F), respectively.



Fig. 2 XRD pattern of (A)  $Fe_3O_4$ , (B)  $Fe_3O_4$ –LD, and (C)  $Fe_3O_4$ –LD–Cu nanocatalyst.

 $30^{\circ}$  can be attributed to the amorphous material coated on the magnetic nanoparticles.<sup>30</sup> According to the XRD results, it can be concluded that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were successfully coated with LD and LD–copper. The XRD pattern clearly depicts that there is no change in the topological structure and in the inherent properties of Fe<sub>3</sub>O<sub>4</sub> before and after the coating with LD. On assessment of the diffractograms of LD–encapsulated and LD–copper complex grafted nanoparticles, the very distinguishable FCC peaks of the magnetite crystal were not changed, which means that these particles have phase stability, but there is a slight decrease in the intensity with broadening of the corresponding peak of LD (Fig. 2C). This can be attributed to the lowering of the scattering contrast between the walls of the Fe<sub>3</sub>O<sub>4</sub> framework and the organic moiety attached over Fe<sub>3</sub>O<sub>4</sub>.

also shows that different reaction conditions during the synthesis did not affect the crystallinity and morphology of the  $Fe_3O_4$  nanoparticles throughout the process.

Fourier transform infrared spectroscopy (FT-IR) seems to be the best technique to characterize the functionalization and modification of magnetic nanoparticles. The FT-IR spectra of the LD, Fe<sub>3</sub>O<sub>4</sub>-LD, and Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocomposites were recorded to confirm the modification of the magnetite surface with the LD and metal ions (Fig. 3A-C). The IR spectra of LD (Fig. 3A) show a strong peak around 3404  $\text{cm}^{-1}$ , due to the O–H stretching vibrations of catechol, and at 1652 cm<sup>-1</sup>, due to the C=O stretching of carboxylic acids. The presence of magnetite nanoparticles in Fe<sub>3</sub>O<sub>4</sub>-LD is observable by the strong adsorption band at about 602 cm<sup>-1</sup>, corresponding to the Fe-O vibrations (Fig. 3B). It is also clear that the strong O-H stretching vibrations of catechol, which are generally present at 3400 cm<sup>-1</sup>, are absent in the spectrum of Fe<sub>3</sub>O<sub>4</sub>-LD (Fig. 3B). Instead, the broad band around 3106 cm<sup>-1</sup> seems to be due to O-H stretching of carboxylic acids. Moreover, on moving from LD to Fe<sub>3</sub>O<sub>4</sub>-LD, a significant reduction in the intensity of the O-H stretching and bending vibrations bands is observed. According to Fig. 3B, the successful Fe<sub>3</sub>O<sub>4</sub> surface modification with LD moieties is verified. In terms of Fe<sub>3</sub>O<sub>4</sub>-LD-Cu (Fig. 3C), a red shift of the band at 1652 cm<sup>-1</sup> is observed (1652 cm<sup>-1</sup>  $\rightarrow$ 1623 cm<sup>-1</sup>), which is probably characteristic of the asymmetrical fluctuations of the carbonyl group after interaction with the metal ions. The intensity of the band at 3106 cm<sup>-1</sup>, corresponding to the O-H bond stretching of carboxylic acids of LD (Fig. 3B), decreases in the spectrum of the Fe<sub>3</sub>O<sub>4</sub>-LD-Cu (Fig. 3C), indicating a strong interaction between the oxygen donors and the metal ions. The appearance of new bands in the region of 575 cm<sup>-1</sup> can be attributed to  $\nu$ (M–N), while the stretching frequency bands in the 447 cm<sup>-1</sup> region correlate to c(M–O), which confirmed the coordination through nitrogen and oxygen.31 The FT-IR data confirmed that the nitrogen and



Fig. 3 FT-IR spectra of (A) LD, (B) Fe<sub>3</sub>O<sub>4</sub>-LD, and (C) Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst.

carboxyl oxygen atoms are found to be involved in coordination with the metal ion in complexes. Overall, the IR results suggest that Fe<sub>3</sub>O<sub>4</sub>-LD-Cu was successfully immobilized onto the surface of the magnetic nanoparticles.

The weight percentage of the copper content in the prepared nanocatalyst was obtained using AAS, and sample digestions were carried out in a microwave oven at 500 watt for 10 min with a constant pressure programme with 5 mL aqua regia. The volume of the filtrate was then adjusted to 100 mL using double deionized water. Reference solutions for copper measurements were made with a high degree of analytical purity to obtain the calibration curves. 0.927% copper content in the catalyst was quantified using a calibration curve in duplicate for each sample. Energy Dispersive X-ray Analysis (EDX) also confirms the ratio of 1.20 : 98.80 (Cu/iron oxide) (Fig. 4). The EDX analysis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles indicate that the well-cleaned final product is mostly composed of O and Fe (Fig. 4A), and in the case of Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst, O, Fe, and Cu with no other signal appearing in Fig. 4B.

The magnetic properties of the synthesized  $Fe_3O_4$  nanoparticles,  $Fe_3O_4$ -LD, and  $Fe_3O_4$ -LD-Cu were analyzed by vibrating sample magnetometry (VSM). The field-dependent magnetization curves shown in Fig. 5 indicate the magnetization as a function of applied magnetic field, measured at room temperature. The coercivity values of the  $Fe_3O_4$  nanoparticles,  $Fe_3O_4$ -LD, and  $Fe_3O_4$ -LD-Cu were 74, 73.65, and 71 G, respectively. In spite of these low magnetization values with respect to the magnetization of pure  $Fe_3O_4$  nanoparticles, <sup>23</sup> which are due to the decrease in the surface moments of the magnetite nanoparticles by the diamagnetic LD coating over the  $Fe_3O_4$ nanoparticles and by the grafting of the metal-ligand complex over  $Fe_3O_4$ -LD, it they are still sufficient for magnetic separation by a conventional magnet. The above-mentioned TEM images also confirmed the encapsulation and grafting of the



Fig. 4 EDX patterns of (A)  $\rm Fe_3O_4-LD,$  and (B)  $\rm Fe_3O_4-LD-Cu$  nanocatalyst.

organic layer over the  $Fe_3O_4$  nanoparticles. Another important parameter for the practical applications of nanoparticles is revealed from the enlarged VSM curve shown in Fig. 5D. The hysteresis loops of the powdered materials showed almost negligible magnetic hysteresis, with both the magnetization and demagnetization curves passing through the origin, which clearly indicates the superparamagnetic nature of the materials. Paper



Fig. 5 Magnetization curves obtained by VSM at room temperature for (a)  $Fe_3O_4$ , (b)  $Fe_3O_4$ –LD, and (C)  $Fe_3O_4$ –LD–Cu nanocatalyst, and (d) inset: enlarged image near the coercive field.

This also means that the magnetic material can only be aligned under an applied magnetic field, but it will not retain any residual magnetism upon removal of the field. Thus, the above discussed  $Fe_3O_4$  nanoparticles appear to be suitable as the support for the catalyst.

The Brunauer–Emmett–Teller (BET) surface area of a magnetic Fe<sub>3</sub>O<sub>4</sub>–LD–Cu sample was determined to be as high as 70.41 m<sup>2</sup> g<sup>-1</sup> (ESI<sup>†</sup>). Similarly, the BJH adsorption and desorption cumulative surface area of the pores are 73.36 m<sup>2</sup> g<sup>-1</sup> and 73.06 m<sup>2</sup> g<sup>-1</sup>, respectively (ESI<sup>†</sup>). The Barrett–Joyner–Halenda (BJH) pore size of the NPs was determined to be 14.37 nm, and the total pore volumes 0.253 cm<sup>3</sup> g<sup>-1</sup> (ESI<sup>†</sup>).

In order to provide further evidence of the formation of  $Cu^{2+}$  complex over the iron oxide core and to determine the oxidation state of copper, the XPS resolution copper 2p spectroscopy results of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>–LD–Cu were compared (ESI†). The signals of Cu<sup>2+</sup> were very faint in the XPS spectrum of the Fe<sub>3</sub>O<sub>4</sub>–LD–Cu nanocomposite (Fig. 6), because of the low loading of



Fig. 6 X-ray photoelectron spectra of Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst.

Cu<sup>2+</sup> ions. Nevertheless, for a better understanding of the oxidation state of copper, the binding energy obtained from the catalyst was compared with the Cu<sup>2+</sup>  $2p_{3/2}$  and  $2p_{1/2}$  peak positions. The binding energies of the main peaks are about 934.59 eV and 942.27 eV due to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively. Since these lie within the range given in literature,<sup>32</sup> it can be concluded that the oxidation state of copper in the catalyst is +2.

#### Catalytic activity

Having synthesized and characterized the  $Fe_3O_4$ -LD-Cu nanocomposite, its role as a heterogeneous catalyst was then evaluated for the oxidation of alcohols. The oxidation was carried out with air, as well as with  $H_2O_2$ , as an oxidant. In order to optimize the reaction conditions and to obtain the best catalytic activity, the oxidation of benzyl alcohol was chosen as a model reaction. In this regard, different reaction parameters, such as solvent, temperature, and amount of catalyst, were investigated (Table 1).

It is seen from the Table 1 (entry-1) that the presence of a catalyst is required for the oxidation of benzyl alcohol. In order to investigate the role of  $Cu^{2+}$  in the catalyst, the model reaction was carried out under the optimized reaction conditions in the presence of  $Fe_3O_4$  and  $Fe_3O_4$ -LD as catalysts (Table 1, entry-2). No progress in the reaction was observed even after five hours. Thus, it can be concluded that  $Cu^{2+}$  incorporated onto the magnetic nanocomposite plays a pivotal role in the solvent-free aerobic oxidation, as well as in the  $H_2O_2$  promoted oxidation, of benzyl alcohol.

As far as the effect of solvent is concerned, the model reaction was performed in several solvents, as well as in solvent free conditions (Table 1, entries 3 to 7). It was observed that the best yield and selectivity were obtained when the reaction was conducted under solvent-free conditions (entries 8 and 9). Moreover, the effect of the catalyst amount on the oxidation of benzyl alcohol was also investigated, by varying the amounts of the catalyst (Table 1, entries 8 to 10). As can be seen, when the amount of catalyst was increased from 15 to 25 mg (entries 8 and 9), the product yield increased from 31% to 60% in air oxidation and 52% to 58% in the H2O2 oxidation, which is probably due to the availability of more acid sites. Furthermore, the percentage yield remained stable with between 25 mg to 50 mg catalyst, with a reduction of about 12% in benzaldehyde selectivity, which may be due to over-oxidation of the substrate at high amounts of the catalyst (entries 9 and 10). According to the results, 25 mg was chosen as the optimum amount of catalyst, due to the best yield and selectivity, for the further steps (Table 1, entry 9, Scheme 2).

The influence of reaction temperature on the catalytic activity was investigated by several separate reactions under the same reaction conditions. As represented in Table 1, in air oxidation, the reaction yield does not increase with temperature (entries 11, 12, and 14), but the selectivity to benzaldehyde decreases significantly because of the over-oxidation at high temperatures. In the case of  $H_2O_2$  oxidation of benzyl alcohol, when the temperature increases from 25 °C to 70 °C (Table 1,

Table 1Effects of different solvent, temperature, and amount of catalyst on the aerobic and  $H_2O_2$  oxidation of benzyl alcohol in the presence of $Fe_3O_4-LD-Cu$  catalyst

Entry <sup>a</sup>	Temperature (°C)	Catalyst (mg)	Solvent	Air oxidation		$H_2O_2$ (30% v/v)	
				Conversion (% ±2 by GC)	Selectivity (% $\pm 1$ by GC)	Conversion (% ±2 by GC)	Selectivity (% $\pm 1$ by GC)
1	25-30	_	_	Trace	99	Trace	99
2	25-30	Fe <sub>3</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> -LD	_	20	99	35	92
3	25-30	25	Water	12	88	30	70
4	25-30	25	Ethanol	16	88	20	71
5	25-30	25	Acetonitrile	49	99	48	94
6	25-30	25	Dichloromethane	25	90	22	75
7	25-30	25	Methanol	20	92	35	72
8	25-30	15	Solvent-free	31	99	52	95
9	25-30	25	Solvent-free	60	99	62	96
10	25-30	50	Solvent-free	59	88	60	96
11	50	25	Solvent-free	58	85	72	96
12	70	25	Solvent-free	58	81	95	96
13	70	50	Solvent-free	59	81	95	96
14	90	25	Solvent-free	60	80	95	91

<sup>*a*</sup> Reaction conditions: benzyl alcohol (10 mmol), benzyl alcohol : H<sub>2</sub>O<sub>2</sub> (30% v/v) mole ratio = 1 : 1.1, solvent = 2 mL, reaction time = 5 h, the main by-product was benzoic acid.





entries 9 and 12), the reaction yield also increases from 58% to 95%, with a 96% selectivity of benzaldehyde. According to the results, the reaction temperature of 25 °C to 70 °C appears to be the optimum reaction temperature range for aerobic oxidation and  $H_2O_2$  oxidation, respectively. According to the above, the results in Table 1 entries 9 and 12 are the optimum conditions for the air and  $H_2O_2$  oxidation of benzyl alcohol, respectively (Scheme 2A and B).

In order to assess the efficiency of the NPs further, the quantity of  $H_2O_2$  and the reaction time were also optimized (ESI<sup>†</sup>). After optimization of the reaction conditions (Table 1 and ESI<sup>†</sup>), the catalytic activity of magnetic Fe<sub>3</sub>O<sub>4</sub>–LD–Cu nanocatalyst was further explored with other benzylic alcohols. The Fe<sub>3</sub>O<sub>4</sub>–LD–Cu catalyst exhibited good activity and selectivity in the solvent-free aerobic oxidation, as well as in the H<sub>2</sub>O<sub>2</sub> oxidation of different benzylic alcohols (Table 2). All of the investigated benzylic alcohols with either electron-donating or electron-withdrawing substituents can be oxidized into their corresponding aldehydes in high yields with excellent selectivity (entries 2–13). In all cases, the turnover number (TON) was as high as ~1850 to 2500 for H<sub>2</sub>O<sub>2</sub> oxidation and ~830 to 1700 for the air oxidation of various benzylic alcohols.

The recycling and recovery of used catalyst is one of the most important criteria for industrial based catalyst systems, and gives useful information about the immobilization process and catalytic stability along the catalytic cycles. The reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst in the model reaction (Scheme 2A and B). In order to regenerate the catalyst, after each cycle, it was separated by an external magnet (Fig. 7A) and washed several times with acetone. Then, it was dried in an oven at 60 °C and reused in the subsequent run. The results show that the Fe<sub>3</sub>O<sub>4</sub>-LD-Cu magnetic catalyst could be reused up to seven times with no significant loss of activity/selectivity (Table 3). It should be mentioned that there was very low Cu<sup>2+</sup> leaching during the reaction and the catalyst exhibited high stability even after seven recycles (Table 3). After that, however, the reaction time increased with each successive recycling experiment, rising from 5 h to 6 h finally in air oxidation. A similar result was also obtained in the H2O2 oxidation of benzyl alcohol (Table 3). This may be due to a gradual loss of the catalytic activity of the nanocatalyst with the number of runs, which may be due to various reasons. One of the reasons may be surface modification due to the deposition of matter during the reaction. The HR-TEM images of the nanocatalyst were recorded after the 7th run of air (Fig. 7B) and H<sub>2</sub>O<sub>2</sub> oxidation (Fig. 7C) of benzyl alcohol. The HR-TEM images display an agglomeration of NPs due to deposited matter (Fig. 7B and C).

### $\label{eq:Table 2} \mbox{Table 2} \mbox{ Aerobic and } \mbox{H}_2\mbox{O}_2 \mbox{ oxidation of various benzylic alcohols over } \mbox{Fe}_3\mbox{O}_4\mbox{-LD-Cu nanocatalyst}$

			$H_2 O_2^{\ a} (30\% \text{ v/v})$		Air oxidation <sup>b</sup>	
Entry <sup>c</sup>	Reactant	Product	Conversion/TON	Selectivity	Conversion/TON	Selectivity
1	ОН	СНО	90/2500	96	52/1444	99
2	NO <sub>2</sub> OH	CHO NO <sub>2</sub>	75/2083	79	36/1000	98
3	O <sub>2</sub> N	O <sub>2</sub> N	69/1916	89	30/833	98
4	O <sub>2</sub> N OH	CHO O <sub>2</sub> N	68/1888	92	40/1111	99
5	NC	NCСНО	90/2500	96	59/1638	99
6	H <sub>3</sub> C-	Н <sub>3</sub> С-СНО	92/2555	98	62/1722	99
7	но-	ноСно	92/2550	95	61/1694	99
8	CI-CI-OH	СІСНО	86/2388	96	59/1555	99
9	СІ	СІ	85/2361	96	60/1666	99
10	СІОН	СІ	78/2166	98	52/1444	99
11	Br	Вг-СНО	70/1944	92	49/1361	99
12	Br	Br	72/2000	95	52/1444	99

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			$H_2O_2^{\ a}$ (30% v/v)		Air oxidation <sup>b</sup>	
Entry <sup>c</sup>	Reactant	Product	Conversion/TON	Selectivity	Conversion/TON	Selectivity
13	H H H	H H N N N N N N N N N N N N N N N N N N	72/2000	96	47/1305	99

<sup>*a*</sup> Reaction conditions: alcohol (10 mmol), atmospheric air, 25 mg catalyst (0.02 wt% or 0.003 mmol copper, obtained by AAS for Fe<sub>3</sub>O<sub>4</sub>–LD–Cu), reaction time and temperature, 12 h and 25–30 °C, respectively. Acetonitrile was used as a solvent (when alcohol was solid and air was used as the oxidant) = 2 mL. <sup>*b*</sup> Reaction conditions: alcohol (10 mmol), alcohol :  $H_2O_2$  (30% v/v) mole ratio = 1 : 1.1, 25 mg catalyst, reaction time, and temperature, 12 h and 70 °C, respectively. <sup>*c*</sup> The main by-product was benzoic acid, TON was calculated on the basis of copper ions estimated by AAS, isolated yield after column chromatography, and selectivity by GC.



Fig. 7 (A) Reaction mixture of benzaldehyde (a) before, and (b) after magnetic separation by a simple magnet. HR-TEM of reused magnetic  $Fe_3O_4$ -LD-Cu nanocatalyst after (B) air oxidation, and (C)  $H_2O_2$  oxidation.

Table 3 Air and  $H_2O_2$  oxidation of benzyl alcohol to benzaldehyde over  $Fe_3O_4-LD-Cu$  nanocatalyst under optimum conditions (recycling experiments)

	Air oxidation <sup>a</sup>			$H_2 O_2^{\ b} (30\% \text{ v/v})$		
Cycle	Time (h)	Conversion (% $\pm 2$ by GC)	Selectivity (% $\pm$ 1 by GC)	Time (h)	Conversion (% ±2 by GC)	Selectivity (% $\pm 1$ by GC)
1	5	60	99	4	95	96
2	5	59	99	4	95	96
3	5	60	99	4	94	95
4	5	59	98	4	95	95
5	5	58	99	5	94	94
6	6	59	99	5	94	95
7	6	58	99	6	94	96

<sup>*a*</sup> Reaction conditions: alcohol (10 mmol), atmospheric air, 25 mg catalyst and reaction temperature 25–30 °C. <sup>*b*</sup> Reaction conditions: alcohol (10 mmol), alcohol :  $H_2O_2$  (30% v/v) mole ratio = 1 : 1.1, 25 mg catalyst, reaction temperature 70 °C.

It is evident from Table 4 that the  $Fe_3O_4$ -LD-Cu nanocatalyst is highly efficient in catalyzing the air, as well as  $H_2O_2$ , oxidation of benzylic alcohols and gave products in good yields with a high turnover number (TON) in comparison to previous literature reports.<sup>5,20e,f/23,25d,e</sup> Hence, the catalytic efficiency of the present catalytic system is considered remarkable in terms of the mild reaction conditions, low catalyst costs, short reaction time, high reaction yield, and easy recovery of the catalyst.

#### Hot filtration test

A hot-filtration based leaching test was conducted to exclude any homogeneous catalytic contribution or lixiviation of the catalytic species in the catalyzed reaction. First, an AAS analysis of the post reaction mixture after catalyst separation was conducted. The results revealed that the concentration of Cu(n) ions in the supernatant corresponded to a negligible catalyst leaching (<0.01 ppm), in so far as there was hardly any change in the amount of Cu compared with the fresh catalyst. Table 4 Comparison of the results of the present system with the recently published catalytic systems for the oxidation of alcohols to aldehyde

Entry	Catalytic system	Reaction conditions	% Yield by GC	Ref.
1	Fe <sub>2</sub> O <sub>2</sub> /MPA-PHEA-Cr composite	Oc-hubbling 45 °C 4 h	60	23
2	Cu-NHC-TEMPO	$C_{6}H_{5}Cl.$ 80 °C. air. 15 h	70	20 20e
3	TEMPO/CuCl <sub>2</sub> /bapbpy	<i>t</i> -BuOK, acetonitrile–methanol (2 : 1), rt, air, 7 h	18	20f
4	Nano-γ-Fe <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub> , 75 °C, 12 h	18	25d
5	Polymer supported palladium catalyst	K <sub>2</sub> CO <sub>3</sub> , water, 100 °C, 6 h	99	5
6	Magnetically recoverable Au NP	Toluene, K <sub>2</sub> CO <sub>3</sub> , 100 °C, bubbling O <sub>2</sub> , 6 h	85	25e
7	Our catalyst	(a) Air, 25–30 °C, 5 h	(a) 60	This work
		(b) $H_2O_2$ , 70 °C, 4 h	(b) 96	

### Conclusion

In summary, a facile route to the synthesis of a copper containing  $Fe_3O_4$ -1-3,4-dihydroxyphenylalanine nanocomposite was reported without using any organosilane precursors. This catalyst then catalyzed the oxidation of alcohols with high TON and excellent selectivity. Also, being magnetically separable, the requirement for catalyst filtration after completion of the reaction was eliminated, which is an additional sustainable attribute of this oxidation protocol. The magnetic catalyst exhibited high catalytic activity/selectivity in the solvent-free aerobic oxidation, as well as in the  $H_2O_2$  oxidation, of alcohols. Further investigation and modification are under progress in our laboratory.

### Experimental

### Materials

Benzyl alcohol, other alcohols, FeCl<sub>3</sub>· $6H_2O$ , FeCl<sub>2</sub>· $4H_2O$ , ammonium hydroxide, Cu(NO<sub>3</sub>)<sub>2</sub>· $3H_2O$ , TEA, H<sub>2</sub>O<sub>2</sub>, ethanol, and L-3,4-dihydroxyphenylalanine (LD) were purchased from Merck Mumbai, India. All the solutions were prepared using double-distilled and demineralized water.

#### Synthesis of magnetic nanoferrites

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by a co-precipitation method as reported previously.<sup>28</sup> FeCl<sub>3</sub>·6H<sub>2</sub>O (6.95 g) and FeCl<sub>2</sub>·4H<sub>2</sub>O (10 g) were dissolved in 50 mL of deionized water and stirred at 50 °C for 30 min under a nitrogen atmosphere. Then, ammonium hydroxide (25%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 60 °C. The precipitated nanoparticles were separated magnetically, washed with water until the pH reached 7, and then dried under vacuum at 60 °C for 2 h. The obtained magnetic nanoferrite (Fe<sub>3</sub>O<sub>4</sub>) was then used for further chemical modification.

### Surface modification of nanoferrites

Nano-Fe<sub>3</sub>O<sub>4</sub> (1 g) was dispersed in 10 mL water by sonication for 30 min. L-DOPA (1 g) dissolved in 5 mL of water was added to this solution and again sonicated for 2 h. The amino acid functionalized nanomaterial was then isolated by an external magnet, washed with water, and then dried under vacuum at 60 °C for 2 h.

### $Synthesis of nano-Fe_{3}O_{4}-\mbox{-L-DOPA-copper complex} \left(Fe_{3}O_{4}-\mbox{-LD-Cu}\right)$

Amino acid functionalized nano-Fe<sub>3</sub>O<sub>4</sub> (1 g) was dispersed in a water–ethanol mixture (1 : 1). To this, an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (120 mg) was added. Triethyl amine (TEA) solution in water was added dropwise to bring the pH of this mixture to 6. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and then dried under vacuum at 60 °C for 2 h.

# Details of experimental procedure for the Fe<sub>3</sub>O<sub>4</sub>-LD-Cu catalyzed oxidation of alcohol

H<sub>2</sub>O<sub>2</sub> as oxidant. Benzyl alcohol (10 mmol) was heated with 30% v/v H<sub>2</sub>O<sub>2</sub> (11 mmol) at 70 °C in the presence of 25 mg (0.02 wt% or 0.003 mmol copper by AAS) of Fe<sub>3</sub>O<sub>4</sub>-LD-Cu catalyst and stirred at that temperature for 4 h. The progress of the reaction was monitored by thin layer chromatography (TLC). On completion of the reaction, the mixture was cooled to room temperature and the catalyst was removed by an external magnet. The liquid organic product was analysed by a gas chromatograph (GC) to calculate the level of benzyl alcohol conversion and the benzaldehyde selectivity. For isolation, the product was extracted with ethyl acetate. The combined organic layer was washed with water and brine solution and then finally dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent left the crude benzaldehyde with a 96% selectivity, which was then purified by column chromatography over silica gel (ethyl acetate : hexane 5 : 95 v/v) to provide pure benzaldehyde in a 87% vield (<sup>1</sup>H-NMR spectroscopic data provided ESI<sup>†</sup>). The oxidation of other alcohols was carried out in a similar manner.

Air oxygen as oxidant. In a typical reaction, benzyl alcohol (1 mL, 10 mmol) and the magnetic catalyst (25 mg) were loaded into a two-neck round bottom flask. The mixture was then exposed to air to allow oxygen flow into the mixture to initiate the reaction. Afterwards, the reaction mixture was stirred under solvent-free conditions with air oxygen for 4.5 h. The conversion and selectivity were determined by GC. The product was isolated by following the similar workup as above. The oxidation of other alcohols was carried out in a similar manner. In the case of solid reactants, acetonitrile was used as a solvent.

All experiments were repeated three times and the reproducibility confirmed. The products purified by short-path silica gel chromatography (0–25% ethyl acetate in hexane, v/v) were analyzed by gas chromatography (GC) and <sup>1</sup>H-NMR spectroscopy (ESI<sup>†</sup>). The recyclability of the NPs was also tested. The NPs were recovered by an external magnet and washed with water, followed by methanol and again water. Finally, they were dried at 60 °C under vacuum and used directly for the next round of reaction without further purification.

### Characterizations methods

The amount of copper in the catalyst and in the supernatant was estimated by atomic absorption spectroscopy (AAS) on an AA 6300: Shimadzu (Japan) atomic absorption spectrometer using an acetylene flame. The optimum parameters for the Cu measurements are: wavelength = 324.7 nm; lamp current = 2mA; slit width = 0.2 nm; and fuel flow rate = 0.2 L min<sup>-1</sup>. The powered X-ray diffraction (XRD) patterns were recorded with a PanAlytical (model; Empyrean) 'X'PERT-PRO XRPD of Cu Ka radiation ( $\lambda = 0.15406$  nm) on an advanced X-ray power diffractometer. Samples were prepared by pressing dried powder, and the patterns were collected at a scanning rate of 2° per min and  $2\theta$  ranging from 0 to  $80^{\circ}$ . The surface area and porosity of the nanocatalyst were measured by a volumetric adsorption system (Micromeritics Instrument corporation, USA, model ASAP 2010) using N2 adsorption/desorption isotherms at 77 K up to 1 bar. Prior to the measurements, the samples were activated (degassed) by heating at the rate of 1 K min<sup>-1</sup> up to 383 K under vacuum. The temperature, as well as vacuum, was maintained for seven hours prior to the measurements. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, while the porosity was calculated by the Barrett-Joyner-Halenda (BJH) method. High-Resolution Transmission Electron Microscopy (HR-TEM) was carried out using a Jeol (Jem-2100) electron microscope operated at an acceleration voltage of 200 kV. For this purpose, a dry powered sample was dispersed in methanol and ultrasonication treatment was applied to it for 30 min. Afterward, the sample was deposited onto a carbon-coated grid at room temperature and it was allowed to air-dry (about 6 hours). Selected area electron diffraction patterns (SAED) and Energy-dispersive X-ray spectroscopy (EDX/EDS) were also investigated from the electron micrographs. FT-IR spectra were recorded as KBr pellet on a Perkin Elmer RX1 model in the range of 4000-400 cm<sup>-1</sup>. Magnetic measurements were done by a vibrating sample magnetometer (EG&G Model 155 VSM) at room temperature in the range of  $+20\ 000\ \text{to}\ -20\ 000\ \text{G}$ . The surface composition was investigated using an X-ray Photoelectron Spectroscopy (XPS) on VSW X-ray photoelectron spectrometer (UK) using a Mg and Al twin anode X-ray gun with multichannel detector and a hemispherical analyser with a resolution of 1.0 eV. The binding energies obtained in the XPS analysis were calibrated against the C1s peak at 284.6 eV.

The Fe<sub>3</sub>O<sub>4</sub>-LD-Cu nanocatalyst catalyzed oxidation reaction was monitored on thin-layer chromatography (TLC) and gas chromatography (GC). All the products of the reduction of nitroarenes are commercially available and were identified by comparing their physical and spectral data (m.p., TLC (silica gel 60 F254, Merck, Mumbai, India)), GC (Perkin Elmer Clarus 500 GC), and <sup>1</sup>H NMR (BRUKER 400 MHz) with those of authentic samples or reported data.

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