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Graphical abstract



Selective Oxidation of benzyl alcohol with Fe-DDPA using H₂O₂ as oxidant

Highlights

- Formation of non-heme iron (II) catalyst through Fe-S interaction.
- Square pyramidal Fe(II)-DDPA complex formation.
- High activity of Fe-DDPA in benzyl alcohol oxidation.
- Mechanistic study through UV-vis, Raman and ESR study.
- Non-free radical benzyl alcohol oxidation under non-Fenton like condition.

Abstract

Selective oxidation of various aromatic benzyl alcohols to benzaldehydes was found to be catalyzed with 90% conversion and 99% selectivity by an iron (II) catalysts herein designated as Fe-DDPA [DDPA= 3'-disulfanediyldipropionic acid]. The Fe-DDPA catalyst was prepared by a small loading of FeCl₂ into a 2D sheet formed by the supramolecular assembling of DDPA. From both solid and liquid state nuclear magnetic resonance (NMR) spectroscopic study it was evident for the stabilization of the Fe(II) center through Fe-S interaction with the disulfide (S-S) unit of DDPA. DDPA was found to serve as an excellent support to maintain a pH that was required for a radical free oxidation of benzyl alcohol to aldehydes. The catalytic oxidation of benzyl alcohols was found to occur with excellent conversion and selectivity in acetonitrile (CH₃CN) solvent in comparison to various other solvents. From various spectroscopic studies viz UV-Vis, FT-IR and ESI-MS it was ascertained that the CH₃CN interacted with Fe-DDPA to form a [(DDPA)₂Fe(CH₃CN)₂]²⁺ species which then reacted with H₂O₂ to form an intermediate Fe-hydroxoperoxo, Fe^{III}-OOH species. The Fe-OOH further got oxidized to the active Fe^{IV}=O species and was responsible for bringing the high selectivity in the oxidation reaction. The generation of highly unstable Fe-OOH species was further confirmed by electrochemical study, UV-Vis, Raman and ESR spectroscopic analysis.

Keywords: Fe-DDPA, Hydrogen Peroxide, Benzyl Alcohol Oxidation, Non-Free Radical Mechanism

1. Introduction

Iron-sulfur clusters or such high potential iron proteins (like ferredoxins, rubredoxins) are one of the important classes of metalloenzymes playing a pivotal role in various electron transfer processes [1]. Their ability to access variable oxidation states under different biological conditions makes them suitable redox-active centers [2]. Because of which they are known to participate in different electron-transfer processes and are also involved in various enzymes like carbon monoxide dehydrogenase, hydrogenases, nitrogenases, etc. activating the small molecules like carbon monoxide (CO), hydrogen (H₂) and nitrogen (N₂) [3, 4 5, 6]. Inspired by the switchable redox behavior of such metal clusters, different iron-sulfur model systems have been developed to mimic the structural, electronic, electron-transfer mechanism and catalytic behaviors [7]. In this regard, thiols and their derivatives have been extensively used to synthesize different iron-sulfur complexes with varied structural diversity and reactivity. For example, Wang et al. [8] reported for synthesis of disulfide bridged co-ordinated dinuclear Fe(II) species and its interconversion to Fe(III) thiolate mononuclear complex in different solvents. Lippard and his co-worker synthesize tetrathiolato Iron(II) complexes for nitrous oxide (NO)-binding [9]. Chen et al. [10] prepared tetranuclear iron complex with benzenetetrathiolate for hydrogen production by proton reduction process. Lee et al. [11] also synthesized iron-thiolate complex for NO binding. The reported Fe-S clusters are mostly been studied either for NO binding, nitrogen fixation reaction, dehydrogenation reaction and to understand the electronic properties [9,11]. Catalytic oxidation of organic substrates like benzyl alcohol or the application of such iron-sulfur complexes in other organic transformation reaction is less known in literature [9-11]. The one best known is the benzoin oxidation to benzil by Sun et al. [12] using iron

(II) thiolate complex as catalyst. Subramanian *et al.* Fe(II)-thioglycolate system for complete oxidation of organic contaminants in water [13].

Selective oxidation of benzyl alcohol to benzaldehyde is one of the important reactions due to the high applicability of benzaldehydes in pharmaceutical products [14, 15, 16]. But to the best of our knowledge iron-sulfur complexes has so far been not known to catalyze such reactions. The main problem with Fenton-like catalyst is the free radical generation and chain propagation reaction that hampers the selectivity by producing various side products [17]. Another problem is the regulation of pH that could suppress the free radical generation. Shi et al. [18] has demonstrated that at low pH (~ 1) the reactivity of Fe(III)-catalyst could be controlled for selective oxidation of BA with H₂O₂. Due to the several disadvantages associated with Fenton-like catalyst for selective oxidation reactions, the interest has been driven towards the design of non-heme iron-catalysts [19, 20 21]. Non-heme iron complexes having axially co-ordinated labile groups like water (H₂O), triflate (OTf), acetonitrile (CH₃CN) are often preferred as they avoid the free radical mechanism [22, 23 24]. The catalytic reactions with such complexes were supposed to proceed *via* catalytically active Fe^{IV}=O or Fe^V(O)OH species giving highly selective oxidized product [22-24]. However, most of these reported non-heme iron complexes bear the N-co-ordinations sites [22-24]. The applicability of non-heme iron-sulfur complexes having axially co-ordinated labile groups has so far been not explored for similar kinds of reactions. Therefore, intrigued by the redox activity and the catalytic ability of ironsulfur complexes herein we tried to develop a new iron-sulfur catalyst having an axially co-ordinated labile group and can have control over the pH under Fenton-like conditions.

2. Experimental Sections

2.1. Materials. Anhydrous iron chloride (FeCl₃) was purchased from E-MERCK. 3marcaptopropanoic acid ($C_3H_6O_2S$, 3-MPA) was brought from Sigma-Aldrich. Sodium hydroxide (NaOH) and potassium chloride (KCl) were received from E-MERCK. HPLC grade acetonitrile

 (CH_3CN) and all the solvent used were purchased from E-Merck. Benzyl alcohol and the other substituted relevant alcohols were used as received from Sigma-Aldrich. Hydrogen peroxide (H_2O_2) and tetrabutylammonium bromide (TBAB) were purchased from E-MERCK. Milli-Q water was used in all the reaction mention in the text.

2.2. Preparation of 3, 3'-disulfanediyldipropionic acid, DDPA. The compound was prepared by treating 1 mL of 3-MPA with NaOH in 5 mL of water at room temperature and the reaction mixture was stirred for 6 h in open air, Scheme 1. The white precipitate was filtered, dried under air and finally crystallized in CH₃CN for further characterization. The same white material was obtained within 10-15 min by reacting 3-MPA directly with 30% of H_2O_2 (3-4 mL) in 10 mL of water.



Scheme 1. Schematic representation of the formation of DDPA from 3-MPA.

2.3. Synthesis of iron-loaded DDPA, Fe-DDPA. An aqueous solution of NaOH was added to 1 mL of 3-MPA taken in a 20 mL round bottom flask by maintaining the pH of the reaction mixture in the range of 4-5. The aliquot of FeCl₃ prepared by dissolving 1 g of anhydrous FeCl₃ in 10 mL distilled water was added slowly (100 μ L at an instant) to the above solution. The resultant white precipitate so obtained was filtered, washed with water and dried in an open atmosphere. The material was vacuum dried before characterization. From CHN analysis the %C and %H content was found to be 34.19 and 4.52, respectively. The material was white, sparingly soluble in water (H₂O) and acetonitrile (CH₃CN) and maintains a pH level of 3.8-3.9 in H₂O and 3.3-3.4 in CH₃CN.

2.4. Catalytic Oxidation of Benzyl Alcohols with Hydrogen Peroxide as Oxidant. In a general process, the benzyl alcohol oxidation reaction was performed by stirring a reaction mixture containing 10 mL of CH₃CN, 1 mmol of BA and 3 mmol of H₂O₂. The reaction was performed at

room temperature under air for 3h. The progress of the reaction was monitored by thin-layer chromatography, TLC. The benzaldehydes were isolated in good yield using column chromatography and the products were characterized using ¹H and ¹³C NMR spectroscopy. The % conversion and selectivity were obtained by GC-MS analysis.

3. Results and discussion

3.1. Characterization of DDPA and Fe-DDPA

Both the materials, DDPA and Fe-DDPA were characterized using different spectroscopic and physicochemical techniques. The structure of DDPA was confirmed from X-ray crystallographic analysis and indicated for the oxidation of 3-MPA forming the disulfide (S-S) bond. The structure of the compound was found to be similar to that reported by Prout *et al.* [25] The S-S bond distance was found to be 2.03 Å and C-S-S bond angle was 104.4°. The crystal packing of the molecule (Fig. 1a and Fig. 1b), represented a zigzag ribbon-like structure by interlinking with the neighboring unit through the carboxylate unit of DDPA via intermolecular facial C-O---H interaction (1.82 Å) that usually appears in carboxylic acids (Fig. 1a) [26]. In addition, the parallel structural motifs were found to be interconnected by weak C-H---O and C-H---S interaction forming a 2D sheet-like structure. The O-H and S-H bond distances in these two weak intermolecular interactions were in the range of 2.71 and 3.16 Å, respectively. The presence of H-bonding interaction between the methylene proton and oxygen atom of the carboxylic groups leads to the creation of voids similar to that of the crown ethers (Fig. 1c). The ORTEPs of 3,3'-disulfanediyldipropionic acid with 50% probability ellipsoid is shown in Fig. S1 and the details of the crystallographic parameters are provided in Table S1 as supporting information.

The crystals of iron incorporated Fe-DDPA was found to be fragile and hence was unable to obtain the crystal structure. This was also evident from the thermogravimetric analysis (TGA) showing ~90% weight loss of Fe-DDPA in comparison to ~60% of the same in case of DDPA at

similar temperature ~250 °C (Fig. S2a). Polarizing microscopic images further revealed for the fact that the crystals of DDPA were flat, glassy and harder than the Fe-DDPA (Fig. S2b-S2e). The Scanning Electron Microscopy (SEM) images of DDPA (Fig. S2f) and Fe-DDPA (Fig. S2g) were almost identical suggesting the absence of unwanted species like iron-oxides or hydroxides over the surface of DDPA. The low thermal stability of Fe-DDPA in comparison to DDPA was attributed to the presence of iron (Fe) interfering the weak intermolecular interactions like C-H---S and C-H---O in DDPA [27]. Howie *et al.* [28] also reported for the reduction of hydrogen bonding interactions on the introduction of cations like Cs⁺, Na⁺ into the supramolecular aggregation of dithiocarbamate. Probably in the present case the sulfur (S) atoms were involved in the Fe^{II}---S interactions and thereby affected the original crystal packing of DPPA.



Fig. 1. The structure of DDPA showing a) 2D-sheet like arrangement, b) zig-zag ribbon-like motif and c) creation of voids *via* weak intermolecular interactions.

Powder X-ray diffraction pattern of Fe-DDPA (Fig S3a, black line) was found to be slightly shifted from that of DDPA (Fig S3a, red line) implying the interaction of Fe with DDPA (Fig. S3a).

No additional peak was observed for pure FeCl₂ signifying the absence of surface adsorbed or bulk FeCl₂ on DDPA. The absence of sharp signal especially at 20 values of 32.14° and 35.76° further confirmed for the non-existence of iron-oxide materials like Fe₂O₃ and Fe₃O₄ [29]. The crystallinity of the Fe-DDPA material was found to retain up to 120 °C without any loss of characteristic signal and was evident by comparing the XRD pattern of the same before, (Fig. S3b, black line) and after heating, (Fig. S3b, blue line). Fe-DDPA however on heating above 150 °C transformed to amorphous black material as confirmed from XRD analysis (Fig. S4) [29]. These results were in accordance with our TGA analysis.

The presence of Fe^{II}---S interaction was evident from solid-state ¹³C-NMR spectrum or crosspolarization magic-angle spinning nuclear magnetic resonance (¹³CPMAS-NMR) spectroscopy. ¹³CPMAS-NMR of DDPA shown in Fig. 2a, black line exhibited three sharp signals at 181.4, 44 and 29.2 ppm corresponding to -COOH and two -CH₂ carbon, here represented as CH₂-C (44 ppm) attached to carboxylate carbon and the remaining one as-CH₂-S (29.2 ppm) for carbon directly bonded to S-atom of disulfide, respectively. The same in Fe-DDPA was observed at 180.1, 25.0 and 30.7 ppm (Fig. 2a, red line). The upfield shifting of -CH₂-C carbon by 19 ppm and downfield shift -CH₂-S carbon by 1.5 ppm clearly suggested for the symmetrical interaction of disulfide group with Fe [30]. This was probably possible due to the presence of interstices spaces (see Fig. 1c) caused by the supramolecular assembling of DDPA. The interaction was considered similar to that recently reported by Wang et al [8]. The lowering of thermal stability was thus attributed to the weakening of the C-S bond caused by the interaction between S and Fe. Moreover, the DDPA molecules might have organized themselves to hold the Fe-atom resulting in a less stable and distorted conformation. The peak at ~ 100 ppm in both the spectra was due to spinning side bands (SSB). As there was only minimal change in the chemical shift value of -COOH so this functional group was not considered to interact with Fe. The solution NMR analysis also suggested for similar interactions. The ¹³C-NMR of

DDPA was recorded in DMSO-d₆ while the same for Fe-DDPA was recorded in DMSO-d₆, methanol (CD₃OD) and acetonitrile (CD₃CN) (Fig. 2b-2f). As observed in ¹³CPMAS, the two methylene carbon in DDPA recorded in DMSO-d₆ gave two highly separated ¹³C-NMR signal at 47.9 ppm and 26.9 ppm for -CH₂-C and -CH₂-S, respectively (Fig. 2b). The same in Fe-DDPA was observed at 34.1 and 33.6 ppm (Fig. 2b). The ¹³C-NMR signal of-CH₂-C and-CH₂-S carbon of Fe-DDPA was found at 34.2 and 30.9 ppm, respectively in CD₃CN and at 34.8 and 34.5 ppm in CD₃OD (Fig. 2c). The lowering of chemical shift value for -CH₂-C carbon and downfield shifting of-CH₂-S carbon clearly suggested for the retention of similar interaction in solution as well in solid-state. The proton ¹H-NMR of Fe-DDPA was also recorded in the above-mentioned solvents (Fig. 2d-2f). As expected, the proton signals of the -CH₂- proton attached to S-atom was observed at lower chemical shift value due to S \rightarrow Fe charge transfer transition in comparison to DDPA recorded in DMSO-d₆ and also in CD₃CN and CD₃OD. The chemical shift (δ) values obtained from both solid and solution phase NMR analysis are provided in Table 1 and also compared with MPA. The ¹H-NMR and ¹³C-NMR spectra of MPA recorded in CD₃CN are provided in supporting information Fig. S5-S6. The comparison of the NMR spectrum of MPA with DDPA are shown in Fig. S7-S8. The absence of S-H proton signal in DDPA and the difference in chemical shift value was a clear indication for the dimerization of MPA through S-S bond formation. It can be seen from Table 1 that the peak separation values ($\Delta\delta$) between CH₂-C and CH₂-S was significantly low in Fe-DDPA compared to DDPA. This implied the existence of strong interaction between the S atom of disulfide bond and Fe. The NMR- spectra of DDPA and Fe-DDPA with proper integration are given in SI, Fig. (S9-S16).

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Fig. 2. a) ¹³C PMAS spectra NMR of Fe-DPPA (red line) and DDPA (black line), b) ¹³C NMR spectra Fe-DPPA (red line) and DDPA (black line) recorded in DMSO-d₆, c) ¹³C NMR spectra Fe-DPPA recorded in CD₃OH (blue line) and CD₃CN (brown line) and d) ¹H NMR spectra Fe-DPPA (red line) and DDPA (black line) recorded in DMSO-d₆, e) ¹H NMR spectra Fe-DPPA in CD₃OD (red line) and CD₃CN(black line), f) shows the peak separation in proton signals recorded in different solvent, pink is for DDPA in DMSO-d₆, red, black and blue are those for Fe-DDPA in CD₃OD, CD₃CN and DMSO-d₆. The broad signals are from solvent water.

	Phase		¹³ C δ in ppm					
Compound	Solid/liquid	Solvent	СООН	-CH ₂ -C	-CH ₂ -S	Δδ in ppm		
DDPA	solid	-	181.4	44	29.2	14.8		
Fe-DDPA	solid	-	180.1	25.0	30.7	-5.7		
MPA	liquid	CD ₃ CN	175.1	38.3	19.7	18.6		
DPPA	liquid	DMSO-d ₆	173.1	47.9	26.9	21		
Fe-DPPA	liquid	DMSO-d ₆	172.2	34.1	33.6	0.5		
Fe-DPPA	liquid	CD ₃ OD	175.4	34.8	34.5	0.3		
Fe-DPPA	liquid	CD ₃ CN	173.4	34.2	30.9	3.3		
¹ H-NMR δ in ppm								
Compound Phase Solvent COOH -CH2-C -CH2-S Δδ in					Δδ in ppm			
MPA	liquid	CD ₃ CN	-	2.61	2.68	0.07		
DPPA	liquid	DMSO-d ₆	-	2.6	3.3	0.7		
Fe-DPPA	liquid	DMSO-d ₆	12.3	2.5	2.8	0.3		
Fe-DPPA	liquid	CD ₃ OD	_	2.7	2.9	0.2		
Fe-DPPA	liquid	CD ₃ CN	-	2.7	2.9	0.2		

Table 1. Chemical shift values of DDPA and Fe-DDPA from ¹³CPMAS and solution phase ¹³C and ¹H NMR in different solvent.

* $\Delta\delta$ =[(CH₂-C)-[CH₂-S)]; for carbon; * $\Delta\delta$ =[(CH₂-S)-[CH₂-C)]; for proton

The non chelation of Fe with the carboxylic group of DDPA was also clearly evident from FTIR and Raman analyses (Fig. S17a-b and Fig. S18). The -COOH vibrational bands were found to remain intact in Fe-DDPA without any significant shift when compared to those of DDPA and MPA, (Figure S17b). In case of both DDPA and Fe-DDPA the va(COO) and vs(COO) vibrations respectively were observed at 1698 and 1424 cm⁻¹ and were found to be slightly shifted from those in MPA appearing at 1714 and 1426 cm⁻¹. The details of FTIR and Raman analysis are provided in supporting information. Literature reports predicted that MPA can either interact covalently or by ionic interaction with metal like Fe [31]. Some earlier studies also found the co-ordination of MPA with iron by bridging between two Fe-centers [32]. However, in the present case, no such bridging mode of –COOH unit was observed in the FTIR or in the Raman spectra. But from our study, it was revealed that the MPA undergoes an oxidation process to form disulfide bond and thereby reduced the Fe(III) to Fe(II). The Fe(II) species was then trapped by DDPA through Fe---S interaction. The

presence of Fe---S interaction was also evident from diffuse reflectance spectroscopy (DRS) analysis (Fig. S19). In the DRS spectra of DDPA a single electronic transition was found at ~210 nm originated from carbonyl group (>C=O) of carboxylate moiety (Fig. S19, blue line). In Fe-DDPA three prominent bands were found at 215, 252 and 350 nm (Fig. S19, red line). The peak at ~350 nm was due to a charge transition from S \rightarrow Fe.

Based on the above spectroscopic analyses a possible binding mode of Fe with DDPA is proposed herein (Fig. 3a). The coordination sphere around Fe was supposed to be surrounded by four sulfur atoms of DDPA while one of axial coordination sites was probably occupied by the Cl⁻ ligand forming a square pyramidal geometry. One of the Cl⁻ ion satisfied the secondary valency maintaining the +2 state of Fe, Fig 3a. The square pyramidal geometry was proposed as most of the complexes of Fe(II) with disulfides and thiol coordinated through sulfur atom are reported to adopt such geometrical arrangement [8,33, 34 35]. In order to substantiate and to understand the possibility of interaction between Fe and S, density functional theory calculation was performed. The initial coordinates of the DDPA was taken from the crystallographic data. The geometry of Fe-DDPA was optimized using triple zeta basis set with sufficiently polarized and diffused function, 6-311++G(d,p)combined with Becke Three Parameter Exchange and Lee, Yang and Parr correlation functional (B3LYP) [36] implemented in Gaussian 16 suit programme [37]. From the Density Functional Theory (DFT) calculations also the square pyramidal geometry with the four S-atoms occupying the four corners of the plane and the Cl⁻ ligand at the axial positions (Fig. 3b) was found to be much energetically favorable and stable one. and the details are provided in the supporting information. The calculated Fe-S bond distances were found to be in the range of 2.28-2.30 Å and the Fe-Cl bond distance was found to be 2.23 Å. The calculated bond distances were found to match with those observed by Wang *et al.* [8]. The highest occupied molecular orbital (HOMO), Fig. 3c was mostly located at the Fe and Cl while the lowest unoccupied molecular orbital (LUMO) was concentrated at

the DDPA and Fe (Fig. 3d). This type of mononuclear Fe pentacoordinate thiol based systems are already reported in literature [33-35,38, 39]. However, to the best of our knowledge, the disulfide coordinated complexes of iron (II) are very less [8]. Hence, Fe-DDPA might find application similar to those of other Fe-S compounds



Fig. 3. a) Plausible structure of Fe-DDPA, b) optimized geometry of Fe-DDPA, c) and d) represents the HOMO and LUMO orbitals of Fe-DDPA. Grey colour is for carbon atoms and red for oxygen atoms, yellow for S atoms.



Fig. 4. XPS spectra of Fe-DDPA a) iron (Fe), b) chlorine (Cl), c) oxygen (O), d) sulfur (S) and e) carbon (C).

The +2 oxidation state of Fe in Fe-DDPA was predicted from XPS analysis. As shown in Fig. 4a on curve fitting the Fe (2P_{3/2}) region, multiple peaks were observed with binding energies (B.E.) of 708.8, 710.7, 712.5 eV and a shakeup satellite peak around ~714.1 eV [40, 41]. These binding energy values were characteristics of Fe-compounds in the +2 oxidation state. The peak at 708.8 eV was attributed to the electron-deficient Fe²⁺ sites caused by the breaking of Fe-S bonds. Similar B.E. values were also observed by Uhlig *et al.* [42] in marcasite. Based on XPS analysis the oxidation state of Fe in Fe-DDPA was found to be +2. Yamashita *et al.* [43] also observed similar B.E. values for Fe(2p_{3/2}) region for Fe²⁺ in Fe₂SiO₄. They found the satellite peak nearly at 718.8±0.1 eV for Fe in +3 oxidation (in Fe₂O₃) while the same for Fe in +2 state (in Fe₂SiO₄) was observed at 714.6±0.2 eV. Mullet also found the B.E. for Fe²⁺ in green rust (GR) at 708.4±0.1 and 710.5±0.2 eV [1]. As the B.E. values of Fe(2p_{3/2}) region in Fe-DDPA was mostly matching with those of the reported values for +2 oxidation of iron so it was confirmed that the Fe in Fe-DDPA was in +2 oxidation state. The

XPS spectrum of Cl2p shown in Fig. 4b represented spin-orbit doublets for Cl atom. The sharp and intense peak at 197.8 eV for Cl($2p_{3/2}$) and 199.4 eV ($2p_{1/2}$) with a separation of 1.6 eV was attributed to inorganic Cl⁻ anions [40]. The splitting of both the energy state giving rise to satellite peak at higher binding energy region of 198.4 eV ($2p_{3/2}$) and 200.02 eV ($2p_{1/2}$) suggested for the sharing of the Cl⁻ electron density with Fe(II). The binding energies values of Cl⁻ were found to match with those reported by Wang *et al.* [40] for FeCl₂ intercalated into graphite layers. The binding energy for Ols at 531.6 eV was for oxygen atom of –COO (-C-O) and that at 532.7 eV was for C=O of carboxylic acid (Fig. 4c) [45]. The binding energy for oxygen was not observed below 530 eV confirming the absence of any iron oxide material or co-ordination of Fe with carboxylate ligand. The S($2P_{3/2}$) and S($2P_{1/2}$) energy levels were found at 162.8 eV and 163.8 eV (Fig. 4d) [46]. The carbon (C1s) binding energy was found at 284.4 eV for C-C and 288.6 eV for O-C=O (Fig. 4e) [42].



Fig. 5. a) Cyclic voltammetry of the DDPA in water by purging N_2 , b) cyclic voltammetry of the Fe-DDPA recorded without N_2 flow (black line) and absence of nitrogen (red line) in water, c) cyclic voltammetry of the Fe-DDPA material recorded in CH₃CN by purging N_2 with TBAB as a supporting electrolyte and d) UV-vis spectra of the Fe-DDPA material in presence of CH₃CN and TBAB.

The presence Fe(II) species in Fe-DDPA was also ascertained from electrochemical analysis. The cyclic voltammogram (CV) of DDPA exhibited two oxidation peaks at 0.15 V and 0.38 V and a reduction peak at 0.23 V (Fig. 5a). The oxidation peak at 0.38 V was matching exactly with that reported for cystine oxidation [47]. The CV of the Fe-DDPA recorded with and without purging N_2 is shown in Fig. 5b. The anodic peak at -0.04 (-0.07) was for oxidation of Fe(II) to Fe(III) while its corresponding cathodic peak was observed at -0.27 (-0.29) V [48]. The peak at 0.32 V and 0.17 (0.29) V were for DDPA and got shifted to lower value due to the presence of Fe(II) chlorides (Fig. 5a). The sharp irreversible peak at 0.66 V was for Cl⁻/ClO₃⁻ couple (Fig. 5b) [47]. On purging N₂ the peak at 0.66 V almost disappeared completely and the new feeble peak was observed at 1.03 V. The other peaks although got shifted but were less influenced by air. This change in potential values allowed us to suggest that the redox behavior of Fe-DDPA especially the Cl^{-}/ClO_{3}^{-} couple was highly sensitive to the presence of atmospheric oxygen. The results of the CV-study were in good accordance with the Pourbaix diagram for Fe and Cl⁻ species at acidic pH (3-4) [49]. Based on the CV result it was found that Fe in Fe–DDPA was mostly in the +2 oxidation state. On performing the CV in CH₃CN with TBAB as supporting electrolyte a strong signal at 0.84 V was observed due to Br⁻ /Br₂ couple (Fig. 5c) [50]. The UV-Vis spectrum of the light yellowish solution resulted from the reaction of Fe-DDPA with TBAB in CH₃CN also showed three bands at 386, 423 and 464 nm. The peak at 386 nm was due to Br₂ species and the other two bands were attributed to charge transfer transition of [C₁₆H₃₆N]₂[FeBr₄] (Fig. 5d) [51, 52 53]. Based on this analysis in CH₃CN in presence of TBAB the following reactions might take place in solution [51].

$$FeCl_{2} + 6CH_{3}CN + 2 [C_{16}H_{36}N]Br \longrightarrow [Fe(CH_{3}CN)_{6}]Br_{2} + 2[C_{16}H_{36}N]Cl$$

$$TBAB$$

$$[Fe(CH_{3}CN)_{6}]Br_{2} + 2[C_{16}H_{36}N]Br \longrightarrow [C_{16}H_{36}N]_{2}FeBr_{4} (423, 464 nm)$$

$$FeCl_{2} + 2[C_{16}H_{36}N]Br \longrightarrow 2 [C_{16}H_{36}N]Cl + Br_{2} + Fe^{2+}$$

$$Fe^{2+} + Br_{2} \longrightarrow Fe^{3+} + Br^{-}$$

In addition to the XPS and CV analysis, the +2 oxidation state of Fe in Fe-DDPA was also confirmed from the phenanthroline test. Usually, Fe (III) compounds do not show this until it is reduced to Fe(II) by hydroxyl-ammine hydrochloride. But in the present case, the phenanthroline test was found to be positive giving deeply colored red-complex in absence of external reducing agent. This also helped us to estimate the Fe-content in Fe-DDPA by colorimetric estimation. The aqueous solution of Fe-DDPA also gave positive silver nitrate (AgNO₃) test indicating the presence of Cl⁻ ions. The amount of Fe in 20 mg of Fe-DDPA dissolved in 50 mL water was estimated by iron-detection test with 1, 10-phenanthroline following the reported procedure [54]. The amount of Cl⁻ ion was calculated with respect to silver chloride (AgCl) precipitation with AgNO₃ from 20 mg of Fe-DDPA dissolved in 10 mL of water. The calibration curve and the UV-Vis spectrum used for iron estimation are provided in Fig. S20. Results predicted the presence of 0.05 mg of Fe(II) and 0.037 mg of Cl⁻ giving an approximate 1:1 mole ratio of Fe(II):Cl. This implied that probably there was one chloride ion out of the coordination sphere of Fe.

3.3. Catalytic Study

Oxidation of benzyl alcohol (BA) to benzaldehyde without the formation of benzoic acid still appears to be one of the challenging reactions [55]. Generation of hydroxyl free radical ($^{\circ}$ OH) from H₂O₂ leading to uncontrolled oxidation of organic products like BA is one of the major drawback [16]. The problem associated with such free radical assisted BA oxidation has been overcome by the use of precious metals like Pd, Au, Ag that participated in benzylic C-H bond activation without following the free radical path [17,56, 57]. Recently, it was also found that metals like Ag can

stabilize the transition state of BA oxidation by participating in Ag- π interaction [14]. Despite being gaining the controlled over the radical mechanism, the fate of the reaction is still doubtful as sometimes the small leaching of Pd, Ag or Au nanoparticles retards the catalytic reaction [17,56,57]. Apart from this, the use of such costly metals or catalyst is also not beneficial for large scale productions [54,55]. Therefore, there still remains scope for low-cost catalyst or material that could overcome the problem associated with BA oxidation with H₂O₂ [58, 59, 60]. In this regard, Fe is considered to be one of the cheapest metals that can be employed for various organic transformation reactions [18-21]. Non-heme iron(II) catalyst are although superior but difficult to synthesize [23,24]. Hence, designing of low valent Fe(II) catalyst without going for ligand synthesis can be a new approach in the field of homogeneous catalysis. Commonly available iron salts have been known to catalyze many organic reactions in presence of some costly reagents or additives [61]. But the same iron salts lead to polymeric tar formation in presence of H₂O₂ leading to uncontrolled oxidation [18]. The Fenton-like systems are therefore limited to organic waste management treatment or so-called advanced oxidation process (AOP) [62, 63].

Another problem in BA oxidation is the requirement of high temperature (>60 °C). The oxidation of BA was also reported with H₂O₂ above 80 °C [64]. Therefore, it is reasonable to find catalysts that still operate at room temperature retarding the non-catalytic and non-selective BA oxidation. Only a few reports are available that accounts for the room temperature oxidation of BA [65]. Both Ghosh and Panda *et al.* synthesized $Fe^{V}(O)$ complex with biuret modified tetra-amidomacrocyclic ligands (Fe-TAML) for room temperature selective oxidation of benzyl alcohol to aldehyde proceed *via* the formation of $Fe^{IV}(O)$ -porphyrin^{*+} intermediate [66, 67]. Liu *et al.* reported that conversion of BA to benzaldehyde with 100% selectivity in the presence of Pt/BiOCl-Al₂O₃ catalyst at room temperature in 3h [68].

As from the above analysis it was evident that Fe-DDPA had a pH within the range which is suitable for non-free radical Fenton-like reaction and hence the material was explored for BA oxidation in presence of H_2O_2 as oxidant. The catalytic reactions were performed at room temperature conditions as the iron (II) species readily gets oxidized under high thermal condition. Fe-DDPA was soluble in both CH₃CN and H₂O that are known to be a suitable solvent for BA oxidation. Therefore, without going for other solvents, the amount of H₂O₂ required for BA oxidation was optimized at room temperature using 10 mL CH₃CN or H₂O as the solvents and 10 mg Fe-DDPA. From the graph shown in Fig. 6a with 3 mmol of H₂O₂, 44% of BA was converted to benzaldehydes with 91% selectivity in H₂O. The conversion and selectivity were found to be 75% and 97%, respectively in CH₃CN with 2 mmol of H_2O_2 after running the reaction for 3 h. On increasing the H_2O_2 concentration above 4 mmol there occurred a substantial decrease in selectivity with almost constant conversion. Thus 2 and 3 mmol of H₂O₂ was considered to be beneficial for the BA oxidation in respective solvents. Catalyst amount also plays a vital role in improving the catalytic conversion of BA. The catalyst amount was varied from 5 mg to 25 mg in both the solvents. It was found that on using 15 mg of Fe-DDPA in H₂O the conversion was improved from 44% to 62% with 90% selectivity. But no improvement was achieved in CH₃CN on increasing the catalyst amount (Fig. 6b). This indicated that the amount oxidant and catalyst was dependent on the solvent. The dependence of the reaction on catalyst amount was also monitored through UV-vis study (Fig. S21). It was found that with the increase in catalyst concentration the formation of benzaldehyde increases linearly showing the first-order rate kinetics. The significant outcome of this analysis was that there was no peak corresponding to benzoic acids (225 nm and 275 nm) clearly demonstrating the high selectivity of the reaction. Usually benzyl alcohol gives an absorption band at 247 nm while benzaldehyde peak appears at 244 nm and 282 nm [22].

The optimum time required for selective and controlled oxidation of BA was also monitored keeping all other parameters fixed, (Fig. 6c). Performing the reaction more than 3h did not influence the selectivity and conversion in both the solvents. So, this amount of period was considered to be the optimal reaction time. To see the effect of solvent on the oxidation of BA to benzaldehyde few other solvents like methanol, ethanol, DCM and chloroform were also examined and the reactions were performed taking 10 mg of Fe-DDPA and 2 mmol of H_2O_2 . The results are shown graphically in Fig. 6d. The selectivity and conversion were found to be less in these solvents in comparison to H₂O and CH₃CN. This might be due to the compatibility of Fe-DDPA in H₂O and CH₃CN acting as true homogeneous Fe(II) catalyst. Further, Fe-DDPA was highly immiscible in dicloromethane (DCM) and chloroform and thereby sluggish the reaction. Thus, from the analysis, CH₃CN was found to the most suitable solvent in terms of conversion and selectivity and also required less amount catalyst and oxidant. As the formation of over oxidized product like benzoic acid is one of the drawbacks of this kind of oxidation reaction, the possibility of formation of such minor products was checked through ¹³C-NMR after an interval of 1h (Fig. S22). Absence of peak near 170-175 ppm for-COOH, appearance of peak around 192 ppm for -CHO group and vanishing of signal at 64.3 ppm for -CH₂ benzylic carbon in the ¹³C-spectra confirmed for the selective oxidation of benzyl alcohol to benzaldehyde.



Fig. 6. Optimization parameters of benzyl alcohol oxidation with Fe-DDPA at room temperature a) amount of H_2O_2 , b) catalyst amount, c) time required in CH₃CN (solid line) and H₂O (dotted line) and d) in different solvent. Blue line for (%) selectivity and black line for (%) conversion. The (%) selectivity and (%) conversion was calculated by GC-analysis.

On optimization of the reaction condition with BA various other substrates were successfully oxidized to their corresponding benzaldehyde (Table 2). All the reactions were performed CH₃CN as some of the substituted BA's were highly insoluble in water. The substituted benzyl alcohols were found to provide high yield and selectivity in comparison to simple BA. In order to see the high selectivity of the reaction, cinnamyl alcohol having both $-CH_2OH$ and C=C unit was considered. In the presence of H₂O₂, the alkenes have high proximity to undergo epoxidation reaction forming epoxides or diol [69]. There are also several studies on the oxidation of C-H and C=C oxidation using non-heme Fe(II) complex proceeding *via* the formation of active Fe-OOH and Fe^{IV}=O species [70, 71]. However, in the present case no such epoxidation reaction occurred and the cinnamaldehydes as well as the chloro substituted cinnamaldehyde were selectively formed (99%) without effecting aliphatic double bond (Scheme 2a, entry 10 Table 2). This was also evident from the crystal structure

of 4-chloro-cinnamaldehyde as shown in Scheme 2b. The ORTEPs of 4-chlorocinnamaldehyde with

50% probability ellipsoid is provided in Fig. S23 and the crystallographic information are in Table S1

of SI. The ¹H and ¹³C NMR of the same are also shown in Fig. S24 and Fig. S25, respectively.

Table 2. Oxidation of various substituted BA's using 10 mg Fe-DDPA and 3 mmol H ₂ O ₂ in 10 m	ıl
CH ₃ CN at room temperature.	

Sl.No	Reactant	Product	% Conv	% Sel	Yield(in mg)	TON	TOF/h
1	ОН		86	99	110	323	116
2	O ₂ N-OH	O ₂ N-	93	99	131	385	128
3	МеО	MeO	85	96	102	300	100
4	MeO	MeO	91	95	110	323	107
5	F	F	81	97	88	258	86
6	ОН		88	97	108	317	105
7	СІОН	CI-CI-CI-CI-CI-CI-CI-CI-CI-CI-CI-CI-CI-C	94	98	120	352	117
8	Br	Br	86	97	147	432	144
9	ОН		93	99	114	335	111
10	СІ	CI	95	99	145	426	142

TON= mg of product/mg of Fe content in 10 mg Fe-DDPA, TOF=TON / time (3h).



Scheme 2. a) Oxidation of cinnamyl alcohol without effecting C=C bond, b) crystal structure of 4-chloro-cinammaldehyde isolated by oxidation of the corresponding alcohol with 99% selectivity.

3.4. Role of Water and Acetonitrile: The above analysis stated that CH₃CN and H₂O served as a suitable solvent for both the catalyst. In order to understand the influence of two solvents, we first considered the change in pH on addition of H_2O_2 to Fe-DDPA (10 mg) dissolved in CH₃CN (black line) and H₂O (red line). The pH was found to decrease with the addition of H₂O₂ (Fig. 7a). This indicated the presence of high concentration of proton in the solution. Shi et al. [18] also demonstrated that at low pH (~1), the oxidation of alcohol occurs via the non-radical Fenton mechanism giving high selectivity in the conversion of BA to benzaldehyde. When BA was added to the solution containing 10 mg of Fe-DDPA and 2-3 mmol of H₂O₂ the pH was found to drop to 0.81 and 0.92 in CH₃CN and H₂O, respectively. This indicated that in CH₃CN and H₂O both the catalyst maintained a pH that was suitable for a non-free radical Fenton like mechanism giving high selectivity in the BA oxidation [62,72]. The influence of H₂O₂ to Fe-DDPA was also compared with FeSO₄.7H₂O. The addition of H₂O₂ also leads to a decrease in pH in case of FeSO₄.7H₂O (Fig. 7a, blue line) but the iron got precipitated out as yellow iron (III) sulfate, Fe₂(SO₄)₃ (Fig. 7a, inset). This further implied the viability of the two catalysts under the prevailing condition. The absence of polymeric tar formation during BA oxidation with Fe-DDPA also signified for the non-free radical pathway (Fig. 7a, inset) [18]. It was observed that other Fe salts like ammonium ferrous sulfate, (NH₄)₂Fe(SO₄)₂·6H₂O, ferric nitrate, Fe(NO₃)₃.7H₂O and anhydrous FeCl₃ proceeded with

immediate formation of polymeric tar in presence of H₂O₂ reducing the conversion and selectivity (Fig. 7b) [18]. DDPA thus helped in maintaining the pH as well as the oxidation state of Fe restricting the shuttling between Fe(II) and Fe(III) and thereby favored the non-free radical mechanism. This statement was validated from the CV study, the CV of Fe-DDPA in water in a saturated H₂O₂ solution resulted in one oxidation peak characteristic of DDPA and sharp cathodic peak at -0.12 V for reduction of Fe(III) to Fe(II) (Fig. 8a) [73]. The absence of any oxidation peak for Fe(II) to Fe(III) implied the inhibition of catalytic cycle between Fe(II) and Fe(III) that allows the production of hydroxyl free radical [70]. On addition of BA, the reduction of Fe(III) to Fe(II) signal was further shifted to -0.28 without any corresponding anodic signal indicated for the non-radical Fenton mechanism [70]. The peak at 0.49 V was due to the oxidation of BA (Fig. 8a). The CV results were in accordance with those reported by Shi *el al.* [18] under acidic condition.



Fig. 7. a) pH variation of Fe-DDPA with different mmol of H_2O_2 in CH₃CN (black line) and H_2O (red line) and FeSO₄.7H₂O in water (blue line) and the solution shown in the inset after addition H_2O_2 , b) Tar formation with $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, $Fe(NO_3)_3.7H_2O$ and anhydrous in presence of H_2O_2 and BA.

The UV-vis study of Fe-DDPA in CH₃CN solvent predicted for the formation of CH₃CN solvated Fe-complex herein we designated as $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ complex. This was evident

from the presence of three signals at 239 nm, 312 nm and 361 nm (Fig. 8b, red line). The peak at 239 nm was from the carboxyl group of DDPA (Fig. 8b, black line) while the other two transitions were for $\pi \rightarrow \pi^*$ transition of CH₃CN and ligand to metal charge transfer transition $d\pi$ (Fe) $\rightarrow \pi^*$ NCCH₃ (Fig. 8b) [74, 75]. On addition of H₂O, the peaks slowly got vanished and ultimately showed the characteristic peak of Fe-DDPA in water (Fig. 8b, blue line) implying the very fast exchange between H₂O and CH₃CN (Fig. 8c). This transition proceeded *via* the formation of intermediate $Fe(OH)^{2+}$ or FeCl₂⁺ species having an absorption band at ~337 nm (Fig. 8c, blue line) [76, 77]. The formation of $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ complex was also evident from FTIR analysis with the presence of v(-C=N) stretching frequency at 2293 cm⁻¹ for lattice co-ordinated CH₃CN and 2256 cm⁻¹ for free CH₃CN (Fig. 8d) [78]. The stretching frequencies were exactly matching with those reported by Rajadurai et al. [78] and they also proposed for the lattice solvation of CH₃CN with Fe(II) complex. The FTIR spectrum was compared with that of pure CH₃CN i.e. the one containing no solute. Although there was no significant shifting in vibrational frequencies but the intensity of the signals at 2293 and 2254 cm⁻¹ were comparatively less than that of CH₃CN. Further, the % transmittance value of Fe-DDPA containing CH₃CN was slightly higher than that of neat CH₃CN. The results indicated that Fe-DDPA in CH₃CN preceded through the formation of [(DDPA)₂Fe(CH₃CN)₂]²⁺ complex while in water probably it formed a $[Fe(H_2O)_6]^{2+}$ or $[(DDPA)_2Fe(H_2O)_2]^{2+}$ complex [22]. The lattice coordination of CH₃CN with Fe was also evident from the ESI-mass analysis with the presence of strong intense signal at m/z value of 577 corresponding to $[(DDPA)_2Fe(CH_3CN)_2]^+$. H₂O. The mass spectrum recorded in CH₃CN is given in Fig. S26 of SI. Recent studies have shown that the redox potential associated with $[Fe(CH_3CN)_2]^{2+}$ or $[Fe(CH_3CN)_6]^{2+}$ species was more favorable for such oxidation process in contrast to the $Fe(H_2O)_6^{2+}$ complex [22]. Probably this might be the reason for giving the better catalytic conversion in CH₃CN in comparison to H₂O.



Fig. 8. a) CV of Fe-DDPA recorded in water after addition of H_2O_2 (black line) and H_2O_2 and BA (blue line), b) UV-vis spectra of Fe-DDPA in CH₃CN (red line) and H₂O (blue line) and DDPA in CH₃CN (black line), c) UV-vis spectra of Fe-DDPA (black line) and after addition of H₂O in the same solution and d) FTIR spectra of Fe-DDPA recorded after dissolved in CH₃CN (black line) and pure CH₃CN (red line).

3.5. Influence of Chloride ion Concentration: Various studies on Fenton-like reactions using Fe(III)- chloride salts predicted that the presence of Cl⁻ ion retards the H₂O₂ decomposition and sometimes produces chloro-substituted product. As the Cl· radical competes with OH radical, the rate of decomposition of organic waste was found to decrease dramatically with increase in Cl⁻ concentration [77]. In the present case, however, no chlorinated product was found but on addition of NaCl (0.5 mL of 0.01M) the reaction became sluggish and up to 24 h, no conversion was observed in TLC. The impact of NaCl was also monitored through UV-vis study. On addition of NaCl solution 10μ L after an interval of 5 min to Fe-DDPA in CH₃CN, the UV-Vis band corresponding to [(DDPA)₂Fe(CH₃CN)₂]²⁺ got vanished with the appearance of a very weak d-d transition at 741 nm

for some unidentified Fe-species (Fig. S27). This truly implied that at high [Cl⁻] concentration retarded the formation of $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ and influenced the catalytic ability of Fe-DDPA. In water, no additional peak was observed for FeCl₂⁺ or FeCl₂⁺ species on the addition of NaCl. Further, the generation of Cl⁻ or Cl₂⁻⁻ was nullified as no oxidation peak corresponding to the couple Cl⁻/Cl⁻ or Cl₂⁻⁻ 2Cl⁻ was observed at 2.41 or 2.09 V (Vs SHE) respectively in CV study [77]. A feeble peak at 0.89 V (1.27 vs SHE) was however observed in the cyclic voltammetry after addition of BA to a mixture Fe-DDPA +H₂O₂ corresponding to oxidation of Cl⁻ for Cl⁻/ClO₃⁻⁻ [48]. Thus it was concluded that under the present condition the amount of [Cl⁻] concentration present in Fe-DDPA did not hamper the catalytic oxidation of benzyl alcohol by competing with H₂O₂ or OH radical.

3.6. Mechanism

From the above physiochemical and spectrochemical analysis, it was clear that the conversion of BA to benzaldehydes occurred *via* a non-free radical Fenton mechanism in the presence of Fe-DDPA and H₂O₂. It is most expected that Fe(II) species will result in the formation of active hydroxyl free radical making the reaction to be non-selective. But in the present case no such retardation in the selectivity was observed. The addition of free radical scavenging agent did not hamper the catalytic conversion suggesting for non-hydroxyl free radical mechanism. Based on these evidences, a probable mechanism is provided in Scheme 3. It was assumed that probably the axially co-ordinated Cl-ligands in Fe-DDPA got exchanged with CH₃CN to forms a redox-active and labile $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ species. Therefore, the present reaction system was compared to that reported by Bataineh *et al.* [22] using iron(II)bis(acetonitrile)bis(triflate), Fe(CF₃SO₃)₂(CH₃CN)₂ as the source of $[Fe(CH_3CN)_6]^{2+}$ species. As CH₃CN was associated as a solvated molecule so they were easily exchangeable with H₂O as evident from our UV-vis study [77]. On addition of 30% H₂O₂, a proton abstraction process took place and the CH₃CN ligands immediately undergo an exchange process with HOO⁻ and H₂O to form a Fe-OOH species as shown in Scheme 3. Prat *et al*

[79] also predicted for similar type of exchange of CH₃CN and triflate (OTf) ligand with H_2O_2 and water in a non-heme Fe(II) complex. As proposed by Prat et al. [79] and many other studies, [22-24] at this stage probably the cleavage of OOH occurs forming a highly reactive $Fe^{IV}=O$ or $Fe^{V}(O)OH$ species (Scheme 3) which then reacted with BA to form benzaldehyde. The interaction of H_2O_2 with Fe-DDPA in CH₃CN was also monitored by UV-vis study (Fig. 9a). Slow addition of H₂O₂ (1µL at a time) initially showed disappearance of peak I (black line) at 239 nm originated from the ligand DDPA. On further addition of H_2O_2 he other two peaks II and III at 312 and 361 nm originated from the charge transfer of $Fe \rightarrow NCCH_3$ started to vanish consecutively one after the other (II followed by **III**, coloured lines) and finally a new peak having a very short lifetime appeared at ~440 nm (peak IV, blue dotted line) corresponding to the $O \rightarrow Fe$ charge transfer transition in Fe-hydroperoxo (Fe-OOH) species (Fig. 9a). The disappearance of peaks at 312 and 361 nm and the appearance of short lifetime peak at 440 nm clearly suggested the replacement of CH₃CN by H₂O and co-ordination of HOO⁻. Laat. *et al.* also reported for appearance of similar band for Fe-OOH species in a similar range [76]. Chen et al. [80] also observed the formation of Fe-OOH species after addition of large excess of H₂O₂ (>50equivalent) and characterized by UV-Vis and Raman studies. The generation of Fe-OOH species was also confirmed from the Raman spectroscopy with the appearance of sharp and intense band at 792 cm⁻¹ for O-O vibration of Fe-OOH species (Fig. 9b) [80]. The less intense band for O-O vibration of H_2O_2 further implied the small concentration of unreacted H_2O_2 . From this spectrochemical analysis, it can be assessed that the H_2O_2 first got stabilized by the dimeric layer of DDPA which than slowly interacted with $[Fe(CH_3CN)_2]^{2+}$ unit forming a reactive Fe-OOH species and finally formed Fe^{IV}=O species. The active Fe^{IV}=O species further catalyzed the selective conversion of BA to benzaldehyde as shown in Scheme 3.

Scheme 3. Plausible mechanism of benzyl alcohol oxidation with Fe-DDPA

Fig. 9. a) UV-Vis monitoring showing the interaction of H_2O_2 with DDPA and $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ and formation of Fe-OOH species. The black line was before the addition of H_2O_2 . The coloured lines represented the influence of H_2O_2 on the charge transfer transition of $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ The blue line showing the peak near 440 nm was due to the formation of Fe-OOH species. b) Raman spectrum of the solution after treatment with H_2O_2 in CH₃CN. c) EPR-spectrum after treatment with different concentrations of H_2O_2 in CH₃CN. d) Expanded form of EPR spectrum c) showing the signal with g-value 4.26. For simplicity we represented the $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ complex as $[Fe(CH_3CN)_2]^{2+}$ in the Figure.

Electron spin resonance (ESR) spectroscopy analysis was performed to understand the formation of iron (III) species during the catalytic reaction. Iron (II) species with S=2 state is usually silent in the X-band region of ESR spectrum and difficult to analyze [81]. The high spin (HS) Fe(II) has non-Kramer degeneracy with high ZFS (zero-field splitting) value of the order 5-20 cm⁻¹. The allowed EPR transitions are therefore can only be observed at high-frequency region or in high magnetic field region. Therefore, we could not perform the EPR analysis of Fe-DDPA with our available X-band EPR instrument operating at 9.45 GHz frequency and magnetic field centered at 390 mT. However, the Fe-DDPA treated with 3 mmol H_2O_2 showed signal with g-value of $g_{II} = 4.0$

and $g_{\perp}=3.9$ characteristics of Fe(III) species with S=3/2 state, Fig. 9c [8, 82]. There was also a weak signal at 4.26 corresponding to S=5/2 state of Fe(III), Fig. 9d. The other two g-values at 2.3 and 2.2 indicated that d-shell electron configuration was more than half-filled caused by the charge transfer transition from S \rightarrow Fe. This implied that Fe-in Fe-DDPA on treatment hydrogen peroxide passed through an intermediate Fe(III)-peroxo-species with nearly square pyramidal geometry having a quantum-mechanically admixing spin state of S=3/2, 5/2. Hassett *et al.* [83] also observed similar transition or oxidation of Fe(II) to Fe(III) on treatment with H₂O₂ with g value nearly 4.3. The appearance of EPR signal with g value close to that of S=3/2 state of Fe(III) further suggested the tetragonal distortion and presence weak field ligand at the axial site. The EPR signals were narrow and sharp which further gave a clear indication for the absence of iron oxide species which shows a broad EPR signal with g value 4.3 and above 5.2. The existence of the spin state of S=3/2 was inconsistent with the analysis performed by Wang *et al.* [8] with disulfide Fe(II) complex and also validated our proposed structure in Figure 3.

3.7. Comparison of result with the reported catalyst

The catalytic performance of Fe-DDPA was compared with many other reported iron catalysts for a similar type of oxidation reaction and is depicted in Table 3 [84, 85, 86, 87, 88, 89, 90]. In terms of productivity the results were highly comparable. However, there are additional advantages to our current process. The advantages of Fe-DDPA over other reported systems were mainly a) the catalyst have inherent low loading of iron content leading to high turnover number (TON), b) it remains unaffected from air oxidation c) external additives were not required to control the pH d) the reaction proceeds at room temperature. Moreover, in CH₃CN the reaction proceeded *via* the formation $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ species which was not evident with other iron salts. This indicated that probably the DDPA maintained a pH as well as suitable reaction condition that favored to set up the equilibrium for exchange of H₂O with CH₃CN. As the earlier studies have postulated

that pH, as well as the presence of $[(DDPA)_2Fe(CH_3CN)_2]^{2+}$ compound is highly beneficial for such oxidation process. Therefore, it can be granted that FeCl₂ bound to DDPA through Fe---S interaction could be beneficial non-heme like iron(II) catalyst for selective conversion of BA at room temperature without going for any harsh condition and also without the addition of any costly metal co-catalyst. The most beneficial point was the progress of the reaction by non-free radical mechanism giving high selectivity under Fenton like condition.

Table 3. BA oxidation performed with some of the reported Iron-based catalysts at different reaction									
conditions									
Catalyst	Temp(°C)	Time(h)	Oxidant	% Con	% Sel	%Yield	Ref		

11.00

Catalyst	Temp(°C)	Time(h)	Oxidant	% Con	% Sel	%Yield	Ref
Iron(II) phthalocyanine	50	3	H_2O_2	63	87.3	55	[19]
[(Tp ^{Ph,Me})Fe ^{II} (BF)]	rt	8	O_2	-	-	75	[21]
Fe(CH ₃ CN) ₆ ²⁺			O ₃	-	-	70	[22]
Fe-BTC	95	10	O_2	11.3	99		[85]
FeCl ₃ @imine-SiO ₂	80	8	O_2			96	[84]
$Fe(NO_3)_3 \cdot 9H_2O/$	rt	3	air	99	99		[56]
ABNO							
Nano-Fe ₂ O ₃	75	12	H_2O_2	33	97		[18]
$[Fe^{II}(L)Cl_2]$	75	5	O ₂	-	-	92	[86]
Fe/Al-SBA-15	120		H_2O_2	2	99		[90]
$Fe/SiO_2/Al_2O_3$.	rt		^t BuOOH	4.6	100		[89]
FeBr ₃	rt	24	H_2O_2	-	-	91	[87]
Fe(III)/phenanthroline		0.5	H_2O_2	-	98	97	[88]
Fe-DDPA	rt	3	H_2O_2	75	97		This
							work

 $(Tp^{Ph,Me} = hydrotris(3-phenyl-5-methylpyrazolyl)$ borate and BF = monoanionic benzoylformate); 1,3,5-benzenetricarboxylic acid; L=2- (arylazo)-1,10-phenanthroline.

4. Conclusion

In summary Fe(II) chloride bound to DDPA through Fe---S interaction forming a tetragonally distorted Fe(II) sulfur system served as an excellent Fenton like catalyst for selective oxidation of BA at room temperature. The ability of the SAM to maintain the proper pH and the oxidation state of Fe appeared as a suitable catalytic system for non-free radical Fenton reaction of BA with H₂O₂. The binding of CH₃CN and the ability to set up equilibrium between aqua and CH₃CN complex of Fe was one of the significant advantages of this process. Fe-nonheme complex having CH₃CN ligand as labile group is known to form Fe-hydroxoperxo complex and undergo water-assisted O-O cleavage

reaction to form redox-active $Fe^{IV}=O$ species. This particular Fe(II) compound behaved similar to those of Fe(II) non-heme catalyst maintaining the required pH for non-free radical Fenton mechanism. Therefore Fe-DDPA can be ascertained as an alternate low-cost catalyst for selective oxidation of BA with H₂O₂. The high selectivity and it's inactivity towards C=C double bond oxidation further entails the high selectivity of the Fe(II) catalyst.

Supporting Information. Details of physical measurement, crystallographic information's, ORTEPs of 3,3'-disulfanediyldipropionic acid, TGA, microscope images, SEM images of DDPA and Fe-DDPA, XRD of both Fe-DDPA and DDPA, XRD of Fe-DDPA after heating up to 150 °C, NMR spectra of 3-MPA in CD₃CN and DMSO-_{d6}, NMR spectra of DDPA and Fe-DDPA in different solvents, FTIR and Raman analysis of both DDPA and Fe-DDPA, Diffuse reflectance spectroscopy (DRS) spectra of both DDPA and Fe-DDPA, Fe-estimation calibration curve, UV-Vis study of benzyl alcohol oxidation, ¹³C NMR spectra of 4-chloro cinammaldehyde, ESI-MS of Fe-DDPA, UV-Vis study on the effect of [Cl⁻] concentration. NMR data of isolated benzaldehydes.

Conflict of Interest:

We declare no conflict of interest.

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