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Iron Oxalate Capped Iron-copper Nano for oxidative transformation of aldehydes

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An efficient, sustainable and green procedure for the synthesis of selective orthorhombic iron(oxalate) capped Fe-Cu bimetallic oxide nanomaterial [Fe(ox)Fe-CuOx] is developed using sodium borohydride (NaBH₄) reduction of iron(II) salt in presence of oxalic acid at room temperature followed by addition of CuSO₄ in water. The reported method is a cost-effective chemical route for producing [Fe(ox)Fe-CuOx] nano material in gram level with surface area of 78.4 m²/g and pore volume of o.141 cc/g. The [Fe(ox)Fe-CuOx] nanomaterial are found to be useful as a recoverable catalyst for the oxidative transformation of aldehyde to its corresponding ester and acid in presence of H₂O₂.

Introduction:

Amongst various nanoparticles, iron oxide nanoparticle has been of great interest because of their multivalent oxidation states, abundant polymorphism, and the mutual polymorphous changes in nanophase.¹ The easy handling, reasonably low cost, nontoxicity, and environmentally friendly character of iron oxide made it enormously popular as a catalyst and are widely utilized on large scale in laboratory, industrial, and environmental processes to accelerate various reactions including oxidation of carbon monoxide, decomposition of soot and NO_x in diesel exhausts, Fischer-Tropsch synthesis of hydrocarbons, water-gas shift reactions, catalytic oxidations of other various organic compounds, and catalytic decomposition of industrial dyes.² Most of these applications require the iron oxide nanoparticles to be chemically stable, uniform in size, and well-dispersed in liquid media. Towards this, various capping agent, templates was employed to control the size, morphology and phase of metallic and oxide iron nanoparticle.³ Very recently, we have shown an efficient and green protocol for the gram level synthesis of orthorhombic iron(oxalate) capped Fe(0) [Fe(ox)-Fe(0)] nonmaterial using sodium borohydride (NaBH₄) reduction of iron(II) salt in presence of oxalic acid at room temperature in water.⁴ During the course of our study, we have observed the transformation of Fe(0) to Fe_3O_4 after keeping the Fe(ox)-Fe(0) at room temperature in water for a prolonged time (1-2 days) which showed $Fe(C_2O_4)$ capped Fe₃O₄ magnetic nanomaterial [Fe(ox)-Fe₃O₄]. Now, we wanted to use the synthesized Fe(ox)-Fe(0) material for the formation of bimetallic Fe-Cu oxide material. Gratifyingly, we were able to synthesize orthorhombic iron(oxalate) capped Fe-Cu oxide material from the reaction between [Fe(ox)-Fe(0)] and CuSO₄ in water. The synthesized iron(oxalate) capped bimetallic Fe-Cu oxide material [Fe(ox)Fe-CuOx] was well characterized by FT-IR, XRD, SEM, and TEM analysis.

On the other hand, esters are highly attractive building blocks as it can readily be interconverted into a number of other functional groups, and they are frequently employed in industry as fragrances, medicines, or in polymer construction.⁵ The classical route to ester preparation involved the reaction between carboxylic acids and alcohols or in a stepwise fashion from carboxylic acid to acid chloride to ester using strong acids, SOCl₂, CDI, DEAD/PPh₃, DCC etc.⁶ However, these methods have one or more of the following limitations: for example, lack of broad functional group tolerance, use of toxic or hazardous reagents, tedious work-up, difficulty in separation of desired ester from the reaction mixture etc. Towards the search for new environmentally friendly, atom-efficient methods which avoid the use of large amounts of condensing reagents and activators, an attractive approach is the oxidative esterification of the readily available aldehydes with alcohols. In the last two decades, various transition-metal catalysts such as vanadium,⁷ rhenium,⁸ silver,⁹ palladium,¹⁰ ruthenium,¹¹ rhodium,¹² copper,¹³ titanium,¹⁴ iridium,¹⁵ iron,¹⁶ nickel,¹⁷ Zinc¹⁸ calcium and magnesium¹⁹ etc. were successfully utilized for the success of this transformation.



However, to take the necessary step from academic research to industrial application for a wide range of catalytic transformations, the catalytic processes have to be sustainable

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with regard to parameters such as solvent, energy source, substrate scope, separation, and the nature of the catalyst.²⁰ A possible solution for the industrial application of catalyst can be the increased utilization of heterogeneous catalysts on biorelevant metals, such as iron, cobalt, and copper, which would be beneficial with respect to catalyst recycling and engineering.²¹ In this regard, Beller et al. successfully reported reusable Co₃O₄-based heterogeneous catalysts for the direct oxidative esterification of alcohols.²² Very recently, Suzuki et al. reported oxidative esterification of aldehydes with alcohols proceeds with high efficiency in the presence of molecular oxygen on supported gold-nickel oxide (AuNiOx) nanoparticle catalysts.²³ Herein, we presented orthorhombic iron(oxalate) capped Fe-Cu oxide [Fe(ox)Fe-CuOx] material catalyzed oxidative esterification of various aldehyde in combination with H₂O₂ as oxidant in methanol. Upon changing the solvent from methanol to acetontrile, we could able to do oxidative transformation of various aldehyde to its corresponding acids in presence of catalytic amount of [Fe(ox)Fe-CuOx] nanomaterial in combination with H₂O₂. The reusability of [Fe(ox)Fe-CuOx] nanocatalyst was successfully examined seven times with only a slight loss of catalytic activity. Both the oxidative transformation reaction of aldehyde was successfully scale up from 1 mmol to 0.3 mol with appreciable turn over frequency (TOF) and yield.

Results and Discussions

Characterization of Iron-copper Nanoparticle

The synthesized [Fe(ox)Fe-CuOx] nano particle has been characterized by FTIR, XRD, SEM, and TEM analysis. We have recently reported the synthesis of single-phase orthorhombic iron(oxalate) capped Fe(0) [Fe(ox)-Fe(0)] nanomaterial from the aqueous phase room temperature reduction of Mohr's salt, (NH₄)₂SO₄.FeSO₄ with sodium borohydride (NaBH₄) in presence of oxalic acid.⁴ The presence of Fe(0) in the material was confirmed from the XRD pattern of the material and the methylene blue reduction by the material. Now, we wanted to use the reactive Fe(0) for the reduction of other metal like Cu(II). For this, the reaction between previously synthesized [Fe(ox)-Fe(0)]material and CuSO₄.5H₂O was done in water at 50 °C for 16h. During the reaction color of the material turned from blackish to reddish brown. After the completion of reaction, brown nanomaterial was separated from the reaction mixture by centrifugation and washed with water, and dried under vacuum at 100 °C for 36h. The nanomaterial characterization by X-ray diffraction (XRD) confirm the presence of orthorhombic Fe(C2O4), 2H2O and Fe₃O₄, as the peaks in XRD are in good agreement with reported XRD pattern of Fe(C₂O₄), 2H₂O and Fe₃O₄ (Fig. 1). Some of the XRD peaks are well matched with the standard XRD pattern of CuO material, which confirms the presence of CuO in the material. So, we thought that the reactive Fe(0) in the [Fe(ox)-Fe(0)] material first reduced the Cu(II) to Cu(0), which is further oxidized into CuO during the course of the reaction. So, Fe₃O₄ and CuO has been capped by orthorhombic

 $Fe(C_2O_4)$, $2H_2O$ in the brown material [hereafter Fe(ox)Fe-CuOx].



The FTIR spectra of [Fe(ox)Fe-CuOx] nanomaterial was also recorded and compared with oxalic acid, $Fe(C_2O_4).2H_2O$, and [Fe(ox)-Fe(0)] to know the binding behavior of the oxalate with the brown material (Fig. 2). In case of oxalic acid a peak at 1710 cm⁻¹ has been found, which is characteristic for carbonyl group. Other two peaks for C-O and C-C bond of oxalic acid appears at 1260 and 1123 cm⁻¹ (Fig. 2). On the other hand, $Fe(C_2O_4).2H_2O$ shows characteristic peaks at 1636, 1360, 1315, 819, and 493 cm⁻¹. Particularly, the peak at 1636 and 1360 cm⁻¹ were typical for metal carboxylate, in which oxalic acid is acting as a bidentate ligand in $Fe(C_2O_4).2H_2O$. Whereas, the other peak at 1315, 819 cm⁻¹ occur due to C-O and C-C stretching vibration.



Fig. 2 Comparative FT-IR spectrum of Fe(ox)Fe-CuOx with oxalic acid, Fe(ox)-Fe(0) and Fe(C_2O_4).2H_2O.

The FTIR spectra of synthesized Fe(ox)-Fe(0) nanomaterial well matched with $Fe(C_2O_4).2H_2O$, which suggest the presence

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of iron oxalate in the [Fe(ox)-Fe(0)] material. However, the FTIR spectra of [Fe(ox)Fe-CuOx] nanomaterial showed peaks at 502, 819, 1319, 1360, and 1691 cm⁻¹. The peak at 1319 and 819 cm⁻¹ occur due to C-O and C-C stretching vibration of binded oxalate. However, the carbonyl stretching frequency for metal carboxylate slightly shifted to higher region may be due to the relatively weak coordination of oxalate with Fe(II) in [Fe(ox)Fe-CuOx] compared to its parent material. Further, the shape and morphology of the [Fe(ox)Fe-CuOx] were investigated with a scanning electron microscope (SEM). The images of [Fe(ox)Fe-CuOx] material indicate the porous flower like morphology of the material (Fig. 3). Energy-dispersive analysis of X-rays (EDS) spectra of [Fe(ox)Fe-CuOx] nanomaterial in a single flower shows that the atomic percentages of Fe and Cu were 43.93% and 12.07% respectively. Whereas, EDS spectrum of a large area consisting of more than one flower suggest the atomic percentages of Fe and Cu were 46.96% and 10.96%, respectively (Fig. 4). The ICP-OES measurements of all the samples were done after digesting the sample with HCl. The ICP-OES analysis of [Fe(ox)Fe-CuOx] nanomaterial shows the atomic percentages of Fe and Cu were 41% and 9%, respectively (Table 4). On the other hand, oxalate content in the [Fe(ox)Fe-CuOx] nanomaterial was determined from the KMnO₄ titration of unreacted oxalic acid amount during the synthesis of [Fe(ox)Fe-CuOx], which suggest the ratio of iron and oxalate is approximately 3:1.24 So, from above all the analysis the approximate formula of [Fe(ox)Fe-CuOx] nanomaterial is $[(C_2O_4)_{1.6}Fe_{4.6}CuO_4].$



Fig. 3 HR-SEM image of Fe(ox)Fe-CuOx

TEM micrographs of [Fe(ox)Fe-CuOx] nanomaterial showed ultrafine particles with layered structure (Fig. 5). The N₂ adsorption–desorption isotherm and the pore size distribution of [Fe(ox)Fe(0)] and [Fe(ox)Fe-CuOx] material are shown in Figure 6 and 7 and confirm the presence of porous structures in both the material. Upon, the incorporation of CuO in the [Fe(ox)Fe(0)], surface area and the average pore volume is increased, which suggest synthesized [Fe(ox)Fe-CuOx] material is more porous compared to [Fe(ox)Fe(0)] material as is also evident from SEM and TEM analysis.



Fig. 4 EDS spectra of the Fe(ox)-Fe-Cu(Ox). The inset shows the position on which the EDS studies were done.

Now, we were interested to check the catalytic activity of the synthesized material. For this, [Fe(ox)Fe-CuOx] promoted oxidative transformation reaction has been done and elaborated in the next section.



Fig. 5 TEM image of Fe(ox)Fe-CuOx



Fig. 6 Nitrogen adsorption-desorption isotherm of Fe(ox)-Fe(0)

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Fe(ox)Fe-CuOx Promoted oxidative transformation of aldehyde to methylesters and acids

promoted Initially, the [Fe(ox)Fe-CuOx] oxidative transformation reaction of 4-methyl benzaldehyde was chosen as a model reaction for the study. Among all the alcoholic solvents tested, only methanol was effective reaction medium for the formation of methyl ester (Table 1). However in ethanol, ⁱPrOH, and ^tBuOH we failed to detect any ester or acid, which indicate that more bulky solvent hindered the esterification reaction. When we changed the solvent from methanol to acetonitrile, only acid was detected as the major product. Other organic solvent like dicholro ethane, tetrahydrofuran (THF), n,n-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and toluene are also effective for the oxidative acidification of 4-methyl benzaldehyde. But, slightly lower yields were achieved in DMF solvent. [Fe(ox)Fe-CuOx] promoted both the oxidative acidification and esterification reaction of 4-methyl benzaldehyde was tried at room temperature with very low yield of product. The [Fe(ox)Fe-CuOx] esterification reaction was tried with varying catalyst loading. No significant difference was observed when slightly increasing the catalyst loading from 1 to 5 mol%. Low yield of esterification product was observed by using only H_2O_2 , which indicate the necessity of metal ion in the esterification reaction. From screening of solvent, temperature, and catalyst loading the following condition has been optimized: catalyst in combination with 6 equivalent of H₂O₂; methanol as a solvent; temperature 70 °C (Table 1). The esterification reaction was tried with iron and copper salt at the optimized reaction condition. But, moderate to poor conversion was achieved with copper and iron salt. Interestingly, Fe(ox)- Fe_3O_4 or [Fe(ox)-Fe(0)] nanomaterial in combination with H2O2 are poorly active for the esterification of 4-methyl benzaldehyde. We have also tried the esterification reaction with oxalic acid and iron oxalate [Fe(ox)], but in both the cases low yield of ester was achieved. Whereas, under optimized reaction condition, Fe₃O₄ produced only acid in 89%, which indicate over oxidation or Fenton-like reaction in presence of Fe₃O₄ leads to only acid product. Under optimized

reaction condition, the possible Fenton-like reaction in presence of Iron salt and H₂O₂ may leads to acid from aldehyde. Interestingly, we have observed 4-methyl benzoic acid in all the iron salt or nanomaterial promoted reaction of 4-methyl benzaldehyde, which further verifies the possibility of Fentonlike reaction in presence of iron salt and H₂O₂. Under optimized reaction condition, both CuO and Cu₂O promote the esterification reaction to its corresponding ester in good yield. However, in both the cases a little amount of acid was formed.²⁵ When compared to other nano materials, we found superiority of [Fe(ox)Fe-CuOx] material towards the oxidative esterification of of 4-methyl benzaldehyde in methanol at 70 °C in air (Table 2). So, incorporation of copper in the material [Fe(ox)Fe-CuOx] increase the surface area as well catalytic activity of the material as is evident from both the catalyst screening and BET isotherm.



H ₃ C—	- Сно	Fe(ox)-Fe-Cu H ₂ O ₂ Solvent, Reflux	→ ң₀с-√	∕—со₂н н₃с-	Со2сн3
	0.1	1/ 0/18	1a	A . 1 /1 \	2a
#	Solvent	Mol(%)"	Time (h)	Acid (1a)	Ester (2a)
				Yield(%)	Yield(%)
1	MeOH	5	10		94
2	MeOH	2	12		92
3	MeOH	1	12		91
5	MeCN	1	12	92	
6	EtOH	1	12	0	0
7	ⁱ PrOH	1	12	0	0
8	'BuOH	1	12	0	0
7	DCE	1	12	48	
8	THF	1	14	47	
10	DMF	1	16	10	
11	DMSO	1	18	38	
12	Water	1	14	16	
13	Toluene	1	14	56	

H ₃ C-	-Сно -Сата Масон	2O ₂ H ₃	c	₂н н₃с—⟨_	
	Ween	, i tenux	1a	:	2a
#	Catalyst	Mol(%)	Time (h)	Ester(%)	Acid (%)
1	Fe(Ox)Fe-CuOx	1	12	91	
2	Fe_3O_4	5	12		89
3	Fe(Ox)-Fe ₃ O ₄	5	12	32	16
4	Fe(Ox)-Fe(0)	5	12	12	18
5	FeCl ₃ .6H ₂ O	5	12	36	48
6	Fe(Ox)	5	12	14	8
7	CuCl ₂	5	12	22	47
8	CuCl	5	12	11	
9	FeCl ₃ (anhydrous)	5	12	0	0
10	-	_ ^a	12	9	0
11	CuO	5	12	59	15
12	Cu ₂ O	5	12	52	25
13	Oxalic acid	5	12	10	
Read	tion condition: 1 mm	ol aldehyde,	, 0.5 ml of	30% H ₂ O ₂ , 0 70°C ^a Reacti	Catalyst (1-5

mol%) was taken in 3 ml methanol and refluxed at 70°C.^aReaction was done with only 0.5 ml of 30% H_2O_2 .

The catalytic acitivity of [Fe(ox)Fe-CuOx] nanomaterial was compared with other known catalyst. In terms of catalytic

conversion and mol%, superiority of the nanomaterial [Fe(ox)Fe-CuOx] was achieved with other known catalytic system (Table 3).

 Table 3 Comparative activity of Fe(Ox)Fe-CuOx catalyst with known catalyst.

H₃C	сно	Cataly H ₂ C MeOH, F		н ₃ с-Со ₂ н	н₃с-)—со₂сн₃
				1a	2a	
#	Catalyst	Mol(Time	Temperature	Ester	Acid
		%)	(h)	(°C)	(%)	(%)
1	Fe(ox)Fe-	1	12	70	91	
	CuOx					
2	CaCl ₂	10	24	70	42	10
3	MgCl ₂	10	24	70	40	6
4	V_2O_5	5 ^a	2	RT	94	
5	ZnBr ₂	10	24	RT	72	3
Rea	action condition	: 1 mmol	aldehyd	le, 0.5 ml of 30%	H ₂ O ₂ , and c	atalyst (1-

Reaction condition. I minor adenyde, 0.5 m of 50% H_2O_2 , and catalyst (1-10 mol%) was taken in 3 ml methanol and refluxed at 70°C. ^aThe reaction was done at room temperature after addition of all the reagents under ice cooled condition.

For practical applications of such heterogeneous nanocatalyst, lifetime of the catalyst and its reusability are very important factors. For this, a set of experiments was done for the esterification of 4-methyl benzaldehyde using 5 mol% [Fe(ox)Fe-CuOx] nanomaterial in combination with H_2O_2 in MeOH at 70 °C. After the completion of the first reaction, the catalyst was recovered by centrifugation, washed with methanol for 3-4 times and dried in vacuum and used for next set of reaction with fresh reactants under the optimized reaction conditions. Upto 5th catalytic cycle, there is negligible drop down in the yield of the esterification reaction of 4-methyl benzaldehyde. However, at the 6th and 7th cycle, slight drop down in the yield was observed. In terms of TOF, [Fe(ox)Fe-CuOx] catalyst could be reused at least 5 times without any change in its activity (Fig. 8).



Fig. 8 catalytic cycle vs turn over frequency (TOF) and yield plot of Fe(ox)Fe-CuOx catalyzed esterification reaction of 4-methyl benzaldehyde.

The ICP-OES analysis of the used [Fe(ox)Fe-CuOx] nanomaterial after 2^{nd} and 5^{th} cycle was done. No appreciable

change was in iron and copper content was observed after 2nd cycle. However slight drop down in both the iron and copper content was observed in the [Fe(ox)Fe-CuOx] nanomaterial after 5th cycle, which suggested suggests slight leaching of both the metal during oxidation of aldehyde (Table 4).

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Table 4. Iron and copper content in the sample from ICP measurement.					
Material	Fe (wt%) ^a	Cu (wt%) ^a			
Fe(ox)Fe-CuOx	41	9			
Fe(ox)Fe-CuOx (after 2 catalytic cycle)	38	8			
Fe(ox)Fe-CuOx (after 5 catalytic cycle)	33	5			

^aboth the Fe and Cu content was determined from the ICP-OES analysis after digesting the sample with HCl.

The substrate scope of the [Fe(ox)Fe-CuOx] promoted esterification reaction has been tested with various aldehydes (Table 3). Under optimized reaction condition, 4-methyl 4-methoxy benzaldehyde, benzaldehyde, benzaldehyde produced corresponding methyl ester in high yield. The reaction of 2-bromo benzaldehyde at the optimized condition gave only 2-bromo benzoic acid as a product in 29% yield. The sterically bulky bromo group at ortho- position hindered the ester formation in case of 2-bromo benzaldehyde. Aromatic aldehydes substituted with electron-withdrawing groups at the *p*-position such *p*-chlorobenzaldehyde, as pbromobenzaldehyde, and p-nitrobenzaldehyde react slowly to form the corresponding methyl esters in good yields. On the other hand, o-substituted aldehyde such as 2-nitro or 2-fluoro benzaldehyde reacts very slowly to form the corresponding methyl 2-nitrobenzoate and methyl 2-fluoro benzoate only in 12% and 12% conversion under optimized reaction condition. However, at optimized reaction condition 2-choloro benzaldehyde leads to methyl 2-chlorobenzoate in 74% yield. So, hydrogen bonding ability of both nitro and fluoro group with OH may hindered the ester formation and leads to its corresponding acid or acetal in case of 2-nitro or 2-fluoro benzaldehyde. The esterification reaction with other heterocyclic araldehyde like thiophene-2-carbaldehyde went smoothly to its corresponding ester acid in 53% and 39% yield respectively. However the esterification reaction does not proceeds with unsaturated aldehyde like cinamaldehyde even after longer reaction time, which may be attributed to its low electrophilicity, hindered the essential hemiacetal formation in the first step.²⁶ On the other hand, esterification reaction of terephaldehyde leads to its corresponding dimethyl isphthalate in 90% and 3-formyl benzoic acid in 8% yield. The esterification reaction of isophthaldehyde also leads to its corresponding dimethyl terephthalate in 52% and 4-formyl benzoic acid in 20% yield. During the [Fe(ox)Fe-CuOx] promoted esterification reaction, in some cases a minor amount of acid has been observed due to the over oxidation of aldehyde, which further does not proceeds to its corresponding ester.

transformation of aldehyde to ester

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	•				
	R CHO HO2, MeOH, Re			CO ₂ H	
#	Aldehyde	Product ^a	Time	Ester	Acid
			(h)	(%)	(%)
1	4-methylbenzaldehyde	1a	12	91	
2	benzaldehyde	1b	10	78	12
3	4-bromobenzaldehyde	1c	18	99	
4	4-nitrobenzaldehyde	1d	20	81	18
5	2-bromobenzaldehyde	1e	12	0	29
6	2-nitrobenzaldehyde	1f	20	12	41
7	4-methoxybenzaldehyde	1g	12	68	29
8	4-chlorobenzaldehyde	1h	16	99	
9	2-chlorobenzaldehyde	1i	12	74	16
10	4-(trifluoromethyl)benzaldehyde	1j	14	48	
11	3-nitrobenzaldehyde	1k	15	68	31
12	2-fluorobenzaldehyde	11	18	12	86
13	Thiophene-2-carabaldehyde	11	14	53	39
14	Isophthaldehyde	$1m^{b}$	15	90	8
15	Terephthaldehyde	1n ^c	17	52	20
16	Cinamaldehyde	10	20	0	0

Table 5 Substrate scope for Fe(ox)Fe-Cu(Ox) catalyzed oxidative

^aReaction condition: 1 mmol aldehyde, 0.5 ml of 30% H₂O₂, 1 mol% Fe(ox)Fe-Cu(Ox) catalyst (5 mg) was taken in 3 ml methanol and refluxed at 70°C. ^bDimethyl isphthalate in 90% and 3-formyl benzoic acid in 8% yield was observed; 'Dimethyl terephthalate in 52% and 4-formyl benzoic acid in 20% yield was achieved

Furthermore, under optimized reaction condition benzoic acid failed to give any desired methyl ester. Whereas, in esterification of 2-nitrobenzaldehyde, we have observed acetal in GC-MS analysis, which further suggest that esterification reaction proceeds via hemiacetal formation mechanism not via acid (Scheme 2).27



Scheme 2. Fe(ox)Fe-Cu(Ox) promoted reaction of benzoic acid and 2-nitro benzaldehvde

The proposed three step mechanism of the esterification reaction is as follows; firstly, aldehyde reacts with alcohol in presence of [Fe(ox)Fe-CuOx] nanomaterial and form hemiacetal, which further reacts with peroxide complex of Cu(II) to form ester via the elimination of conjugate base of the peracid.



The [Fe(ox)Fe-CuOx] promoted oxidative transformation of aldehyde was further extended to acid by changing the solvent from methanol to acetonitrile. From solvent, temperature, and catalyst mol% screening the following condition has been optimized: 1 mol% catalyst in combination with 6 equivalent of H₂O₂; acetonitrile as a solvent; temperature 90 °C. Under the optimized reaction condition, p-substituted aldehyde like 4methoxy bezaldehyde, 4-methyl benzaldehyde, 4-chloro benzaldehyde, 4-bromo benzaldehyde produced their corresponding acid in good to moderate yield (Table 4). The osubstituted aldehyde like 2-chloro benzaldehyde or 2-fluoro benzaldehyde leads to its corresponding acid in 72% and 88% yield. Whereas, poor yield was achieved in case of 2-nitro benzaldehyde. The [Fe(ox)Fe-CuOx] promoted acidification reaction of isophtahldehyde leads to its corresponding 3-formyl benzoic acid in 25% yield.

transformation of aldehyde to acid	-
Fe(ox)-Fe-Cu	

Table 6 Substrate scope for Fe(ox)Fe-Cu(Ox) catalyzed oxidative

R	CHO H ₂ O ₂ , MeCN, Reflux	R CO ₂ H		
#	R	Product	Time	Yield ^a
			(h)	(%)
1	4-methylbenzaldehyde	2a	10	68
2	benzaldehyde	2b	10	99
3	4-nitrobenzaldehyde	2c	14	91
4	2-nitrobenzaldehyde	2d	14	32
5	4-methoxybenzaldehyde	2e	16	47
6	4-chlorobenzaldehyde	2 f	14	91
7	3-nitrobenzaldehyde	2g	14	95
8	2-chlorobenzaldehyde	2h	15	72
9	2-fluorobenzaldehyde	2i	14	88
10	4-(trifluoromethyl)benzaldehyde	e 2j	14	43
11	Isophthaldehyde	2k	16	25 ^b

^aReaction condition: 1 mmol aldehyde, 0.5 ml of 30% H₂O₂, 1 mol% Fe(ox)Fe-Cu(Ox) catalyst (5 mg) was taken in 3 ml acetonitrile and refluxed at 90°C. b3-formyl benzoic acid in 25% yield was observed.

Application of Fe(ox)-Fe-Cu promoted oxidative transformation in large scale

Now, we were interested to check the activity of [Fe(ox)Fe-CuOx] nanomaterial for the large scale synthesis of ester and acid. For that we have stepwise scaled up the esterification Journal Name

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reaction from 1 mmol to 10 mmol to 300 mmol with varying amount of catalyst loading (Table 5). In 10 mmol scale, 10 mg catalyst (0.2 mol%) was sufficient for the conversion of benzaldehyde to benzoic acid in 85% yield. Further scale up from 10 mmol to 300 mmol with 100 mg of catalyst for benzaldehyde to benzoic acid conversion ended up with 60% yield. We have also tested the esterification reaction of 4methyl benzaldehyde with 100 mg of catalyst in 300 mmol scale, which ended up with mixture of methyl 4-methyl benzoate and 4-methyl benzoic acid in 59% and 25 % yield respectively. On the other hand esterification of benzladehyde in 300 mmol scale leads to mixture of methyl benzoate and benzoic acid in 39% and 30 % yield respectively.

Table 7Substrate scope for Fe(ox)Fe-Cu(Ox) catalyzed oxidativetransformation of aldehyde to acid in large scale.

	R		Sol	(ox)-Fe-Cu (mol%) H ₂ O ₂ , vent, Reflux	CO ₂ Me			
#	R	solvent	Time	Scale	Catalyst	Ester	Acid	
			(h)	(mmol)	(mg)	(%)	(%)	
1	Н	MeCN	20	$10^{\rm a}$	10		85	
2	Н	MeCN	24	300	100		60	
3	Me	MeOH	24	300 ^b	100	59	25	
4	Н	MeOH	24	300	100	39	30	
aRea	^a Reaction condition: 10 mmol aldehyde, 3 ml of 30% H ₂ O ₂ , 10 mg Fe(ox)Fe-							

²Reaction condition: 10 mmol aldehyde, 3 ml of 30% H₂O₂, 10 mg Fe(ox)Fe-Cu(Ox) catalyst was taken in 25 ml of acetonitrile and refluxed at 90°C for required time. ^bReaction condition: 300 mmol aldehyde, 10 ml of 30% H₂O₂, 100 mg Fe(ox)Fe-Cu(Ox) catalyst was taken in 150 ml of acetonitrile/methanol and refluxed for required time.

Experimental Section

Synthesis of [Fe(ox)Fe-CuOx] Nanomaterial:

In a typical procedure, 284 mg of Mohr's salt, $(NH_4)_2SO_4$.FeSO₄ was taken in 150 ml of distilled water in a 500 ml conical flask and 126 mg of oxalic acid, H₂C₂O₄ was added to this and stirred vigorously. In another 500 ml conical flask, a solution of 1.2 g of sodium borohydride, NaBH₄ was prepared in 100 ml distilled water and was added slowly in an earlier prepared solution with vigorous stirring. During the addition, the colour of the solution slowly changed into yellow. After few minutes, when black Fe nano particle began to appear, the NaBH₄ addition was stopped. To this, earlier prepared 100 ml 0.01(M) CuSO4 solution was slowly added to it at 60 °C for 0.5 h. After 5-6 h of addition, the colour of the solution slowly turned to yellowish brown. After 16 h, the reaction mixture was centrifuged, washed 3-4 times with water, collected and dried under vacuum and kept for further application.

General procedure for [Fe(ox)Fe-CuOx] catalyzed oxidative transformation of aldehyde to its corresponding ester and acid:

For the oxidative esterification of an aldehyde, 1 mmol of the aldehyde was dissolved in 3 ml methanol or acetonitrile in a 10 ml round bottom flask. After that, 0.5 ml 30% hydrogen

peroxide (H_2O_2) solution, and required amount of catalyst, [Fe(ox)Fe-CuOx] was added to it and stirred for 5 min at room temperature. The reaction mixture was refluxed at a controlled temperature bath for the required time. The progress of the reaction was monitored by TLC at certain intervals. After the completion, the mixture was centrifuged and the supernatant was collected. Finally, the conversion of the aldehyde to the respective ester or acid was monitored by GCMS analysis.

Instruments

All the samples for FTIR study were properly washed with distilled water at least five times, and then dried under vacuum. Finally, samples for the FTIR spectra were recorded using IMPACT 410 Thermo-Nicolet instrument from a thin transparent KBr pellet. The XRD patterns of the sample was recorded on a Philips PW-1710 X-ray diffractrometer (40 kV, 20 mA) using Cu Ka radiation (k = 1.5418 Å) in the 2 Θ range of 10–90° at a scanning rate of 0.5 ° min⁻¹. The XRD data were analyzed using JCPDS software. Surface morphology of all the samples were recorded by using a scanning electron microscope (JEOL JSM5800) with an accelerated voltage 5-20 kV. TEM images were acquired using JEOL JEM-2010 microscopes with an operating voltage of 200 kV.

Conclussion

In summary, iron(oxalate) capped Fe-Cu bimetallic oxide [Fe(ox)Fe-CuOx] nanoparticle was synthesized using a facile approach. The porous [Fe(ox)Fe-CuOx] material with good surface area and surface volume is found to be useful as a catalyst in presence of H_2O_2 for the oxidative transformation of aldehyde to its corresponding ester and acid in moderate to good yield. In terms of environmental compatibility, reusability, operational simplicity, [Fe(ox)Fe-CuOx] material were very simple, effective and economical. The porous nature of the Fe-Cu bimetallic is also expected to be useful in many other applications.

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Email: <u>spratihar@tezu.ernet.in</u>, <u>spratihar29@gmail.com</u> Experimental details and GC-MS spectra of all the compounds are available in Electronic Supporting Information (ESI)]. See DOI: 10.1039/b000000x

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