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ARTICLE TYPE

Magnetic Copper Ferrite Nanoparticles/TEMPO Catalyzed Selective Oxidation of Activated Alcohols to Aldehydes under Ligand- and Base-Free Conditions in Water †

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A novel, effective and sustainable strategy for the synthesis of aldehydes has been developed using inexpensive, readily available, oxygen-stable and recyclable $CuFe_2O_4$ nanoparticles as the catalyst. The corresponding substituted aldehydes were obtained in moderate to good yields by aerobic oxidation of aromatic alcohols in water under dioxygen atmosphere. Importantly, a ligand or a base was not necessary. The catalyst was completely recoverable with an external magnet and could be reused six times without significant loss of catalytic activity.

Introduction

Direct conversion of primary alcohols to the corresponding aldehydes is still a pivotal reaction in organic synthesis.[1] In traditional oxidation processes, the oxidation of alcohols is accomplished by use of stoichiometric amounts of inorganic oxidants such as CrO_3, $KMnO_4$, SeO_2, hypervalent iodine compounds and toxic heavy metal salts.[2] Unfortunately, these oxidants might lead to the formation of quantities of unfriendly waste in the environment such as non-recoverable toxic by-products, and large volumes of solid waste. In recent years, transition metals such as Pd,[3] Au,[4] Cu,[5] etc., or their corresponding metal complexes have been widely applied in the aerobic alcohol oxidation. As a pioneering work, Nakazawa and co-workers recently reported a first iron-catalyzed method for aerobic oxidation of alcohols to aldehydes.[6] Non-metalcatalytic systems for this oxidation transformation have also been attract much attention,[7] In 2014, Jahn and co-workers reported that TEMPO/*t*-BuONO system can catalyze primary and secondary alcohols to the corresponding aldehydes and ketones, respectively.[8] However, in some cases, most of these methods might suffer from some drawbacks such as the rarity and price transition metal catalyst, ligand together with strong base conditions, metal contamination in the end products and undesirable stoichiometric oxidants, which should still impede their applications on a large scale. Therefore, a more green and effective process is needed.

In view of the principles of green chemistry, the proposal of reaction conditions, media and catalysts, is still challenging in the current chemistry.[9] Since catalysis has a tremendous impact on "green chemistry", optimization of existing chemical transformations together with the development of practical, environmentally friendly processes depend greatly on improvement of catalyst performance.[10] Recently, heterogeneous catalysts have attracted much attention in organic transformations due to their interesting reactivity as well as for economic and environmental reasons. Particularly, a large number of recyclable supported catalytic systems have been developed.[11] For example, Li and co-workers reported an efficient palladium on graphene catalyst for the selective oxidation of aromatic alcohols to corresponding carbonyl compounds.[9f] Very recently, Garcia's group developed an elegant work for the oxidative transformation catalyzed by metal-organic frameworks with the assistance of TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy).[12] Excellent as these works are, the small size of catalyst particles might often make their separation and recycling difficult, and the efficiency of the recovered catalyst might be somewhat reduced as a result of a filtration step.

Recently, magnetic nanoparticles (MNPs) have emerged as ideal catalysts or supports, and have been extensively used in organic transformations because of their easy preparation, large surface area ratio, high dispersion property in organic solvents and efficient separation by using an external magnet and without the need for filtration step.[13] Among all the magnetic nanoparticles, copper(II) ferrite ($CuFe_2O_4$) nanoparticles have emerged as a powerful and excellent catalyst for many organic transformations.[14] Furthermore, from the viewpoint of green chemistry, replacement of conventional hazardous organic solvents by safe and green reaction media has always been a thread in the sustainable chemistry. There is no doubt that, water can be considered as an attractive solvent, because it is easily available, non-toxic and environmentally friendly in the world. Besides that, water is also known to enhance the reaction rates and to affect the selectivity of a lot of organic transformations.[15] In addition, for economical and environmental reasons, there is

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an increasing demand for the use of dioxygen as an ideal oxidant for many oxidation reactions due to its abundance, low cost and nontoxicity. In continuation of our endeavors to develop $CuFe_2O_4$-catalyzed organic transformations,[16] we herein report a green, practical and efficient $CuFe_2O_4$-catalyzed aerobic oxidation of aromatic alcohols to aldehydes by using environmentally benign water as the solvent under dioxygen atmosphere. Notably, when we were performing these studies, Lipshutz and his coworkers reported an elegant example of the direct oxidation of activated alcohols to aldehydes or ketones using CuBr/TEMPO as the catalyst using water as the solvent.[17]

Results and Discussion

The copper(II) ferrite nanoparticles were prepared according to the literature procedure,[18] and were characterized by X-ray diffraction (Fig. 1). The energy-dispersive X-ray spectroscopy shows that the spheres are composed of Cu, Fe and O, as expected (Fig 1, ESI†). Moreover, the diffraction patterns of all the peaks are in agreement with the standard XRD pattern (JCPDS34-0425), so are the ones after three usages. Also, as can be seen from the SEM and TEM images, the $CuFe_2O_4$ nanoparticles could remain well in a similar state, even after third cycles. (Fig 2 and Fig 3).

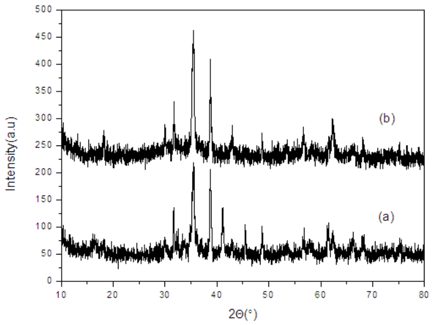


Fig. 1 XRD spectrum of native $CuFe_2O_4$ catalyst. (b) XRD spectrum of reused $CuFe_2O_4$ catalyst after ^{3}th cycle

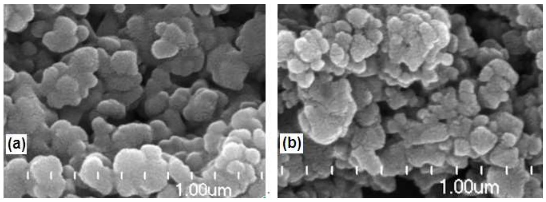


Fig. 2 (a) SEM images of the fresh $CuFe_2O_4$ nanoparticles. (b) SEM image of the $CuFe_2O_4$ nanoparticles after 3th cycle.

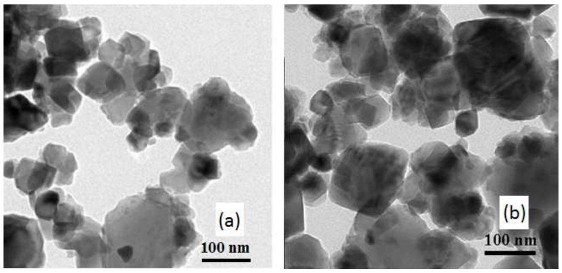
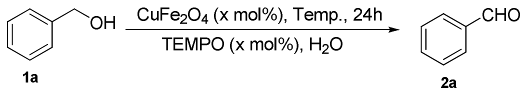


Fig. 3 (a) TEM image of the fresh $CuFe_2O_4$ nanoparticles. (b) TEM image of the $CuFe_2O_4$ nanoparticles after 3th cycle.

Initially, phenylmethanol (**1a**) was selected as the model substrate to optimize the reaction conditions, including the choice of solvent, temprature and the amount of TEMPO under a dioxygen atmosphere (Table 1). Firstly, a range of solvents such as H_2O, Toluene, DMF, DMSO and THF were investigated in the presence of 0.1 equiv of $CuFe_2O_4$ nanoparticles and 6.25 mol % TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) (relative to amount of **1a**) under dioxygen atmosphere (entries 1-5), H_2O and THF gave the highest yield among the solvents tested (entry 1 and 5), and we chose the most green and environmentally friendly water as the solvent. The reason might be the optimum oxygen solubility of water. Besides that, the hydrogen bonding interaction between water and alcohols which could active the alcohols can not be excluded. We attempted different temperature (compare entries 1, 6-8), and 100 °C was optimal. The yield was not significantly improved when the reaction time was prolonged to 48h, at 30°C, 60°C and 90°C respectively. The reaction yield decreased when the amount of TEMPO was lowered (entries1, 9-10). Control experiments confirmed that the desired benzaldehyde was not formed in the absence of the catalyst (entries 11), and it gave a moderate yield under air atmsphere. Considering the importance of bases and ligands in the traditional Cu/TEMPO oxidative systems, we added 2.0 mmol KOH in the standard reaction system, however, the reaction efficiency was not obviously enhanced. The reason might be the large surface area ratio of $CuFe_2O_4$, and make it easy to coordinate with alcohol and TEMPO without bases and ligands(see scheme 1, plausible mechanism) . As a result, the optimized reaction conditions were identified as using $CuFe_2O_4$ nanoparticles(10 mol%), TEMPO (1.25 mol%), H_2O (2mL) at 100 °C under dioxygen atmosphere.

Table 1 Optimization of the reaction conditions[a]

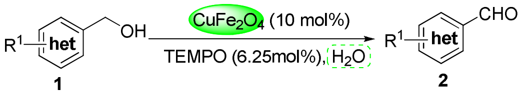


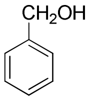
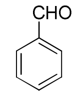
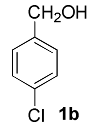
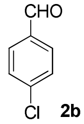
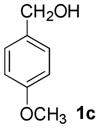
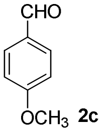
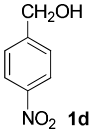
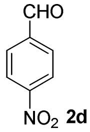
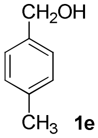
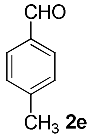
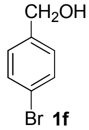
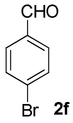
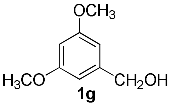
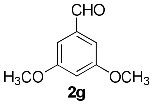
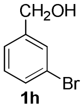
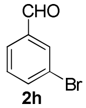
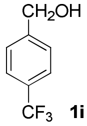
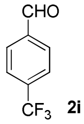
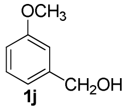
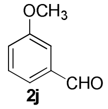
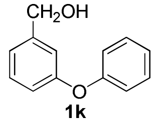
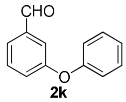
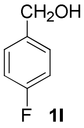
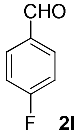
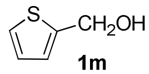
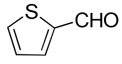
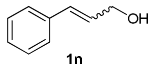
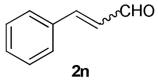
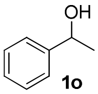
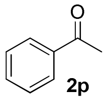
Entry	Solvent	Temp (°C)	Yield (%)[b]
1	**H_2O**	**100**	**95**
2	Toluene	100	40
3	DMSO	100	–[f]
4	DMF	100	–[f]
5	**THF**	**100**	**92**
6	H_2O	30	–[f]–[g]
7	H_2O	60	75, 76[g]
8	H_2O	90	83, 88[g]
9	H_2O	100[c]	75
10	H_2O	100[d]	80
11	H_2O	100[e]	–[f]
12	H_2O	100	64[h]
13	H_2O	100	87[i]

[a] Reaction conditions: Benzyl alcohol (**1a**; 2 mmol), catalyst (0.1 mmol), TEMPO (0.125 mmol), H_2O (2 mL), under O_2 atmosphere. [b] Isolated yield. [c] TEMPO (0.025 mmol). [d] TEMPO (0.05 mmol). [e] No catalyst. [f] Not detected. [g] The reaction time prolonged to 48h. [h] Under air atmosphere. [i] 2.0 mmol KOH was added.

As shown in Table 2, the scope of substrates was investigated, and all the examined substrates provided the corresponding aldehydes in moderate to good yields. For substituted aromatic alcohols, the substrates containing electron-withdrawing groups exhibited higher reactivity than the others. For example, a low yield of the oxidative product (49%) was obtained from (4-nitrophenyl)methanol (Table 2, entry 4). Thiophen-2-ylmethanol (**1m**) was a good substrate in this transformation, and afforded corresponding aldehyde in 62% yield. In addition, 3-phenylprop-2-en-1-ol (**1n**) was also tolerated in this transformation, thus generating **2n** in 85% yield (Table 2, entry 14). Although primary alcohols showed high reactivity, unfortunately, secondary benzylic alcohols were poor substrates (Table 2, entry 15). The cascade reactions could tolerate some functional groups such as methyl, nitro, ether, C-F bond, C-Cl bond and C-Br bond, which could be used for further transformations at the substituted positions.

Table 2 $CuFe_2O_4$-catalyzed synthesis of aldehydes from alcohols [a,b]



Entry	1	2	Yield (%)
1	 **1a**	 **2a**	95%
2	 **1b**	 **2b**	79%
3	 **1c**	 **2c**	86%
4	 **1d**	 **2d**	49%
5	 **1e**	 **2e**	87%
6	 **1f**	 **2f**	84%
7	 **1g**	 **2g**	94%
8	 **1h**	 **2h**	80%
9	 **1i**	 **2i**	66%
10	 **1j**	 **2j**	96%
11	 **1k**	 **2k**	72%
12	 **1l**	 **2l**	79%
13	 **1m**	 **2m**	62%
14	 **1n**	 **2n**	85%
15	 **1o**	 **2p**	trace

[a] Reaction conditions: the substituted alcohols (**1a**; 2 mmol), $CuFe_2O_4$ (0.2 mmol), TEMPO (0.125mmol), H_2O(2 ml), 100 °C, 24 h, under O_2. [b] Isolated yield.

We also studied the recyclability of the catalyst. For this, we investigated the $CuFe_2O_4$-catalyzed oxidation of phenylmethanol (**1a**) to benzaldehyde (**2a**) under the optimized conditions. After completion of the reaction, the reaction mixture was cooled to room temperature, and the catalyst was magnetically separated from the reaction mixture (Fig. 4), washed ethanol/acetone and dried at 100 ^{o}C for 2 h and then used directly for further catalytic reactions. The catalyst showed no significant loss of activity after six cycles as illustrated in Fig. 5. This illustrate a promising approach from sustainable and practical chemistry viewpoints. Then, We investigated the leaching of metal from the $CuFe_2O_4$ nanoparticles. After completion of the reaction, the filtrate was tested by the AES (Atomic Emission Spectroscopy) technique, it was found that the leaching of Cu and Fe in three consecutive cycles was ≤ 0.5 ppm.

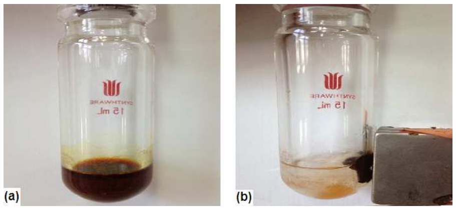


Fig. 4 $CuFe_2O_4$ after oxidation reaction dispersed (a); magnetic separation of the catalyst at ambient temperature with a Nd-Fe-B based magnet (b)

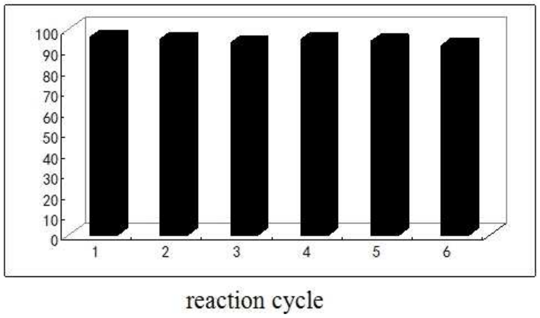
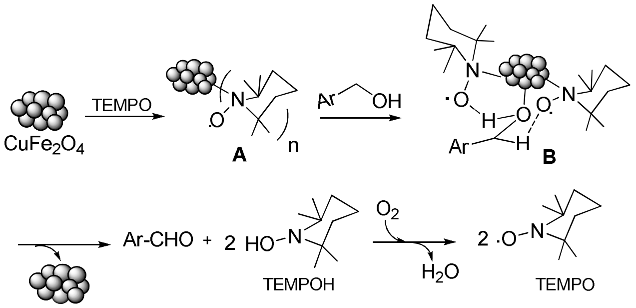


Fig. 5 Yields from recycled copper (II) ferrite catalyst

The control experiments reveal that TEMPO and $CuFe_2O_4$ are indispensable parts of this efficacious catalytic system (entries 1 and 9-11, Table 1). Although the mechanism for the present oxidation pathway is not yet clear, according to the previous report a proposal mechanism would be herein presented (Scheme 1). First, TEMPO coordinate to the $CuFe_2O_4$ nanoparticles to lead to complex **A**. Subsequently, Species **A** in combination with alcohols lead to the formation of the species **B** (In $CuFe_2O_4$, Cu is present as Cu(II) in the crystal lattice, So alcohols and TEMPO might be coordinate to Cu(II), which is consistent with the previous reports[5b,19a]), which was considered as the intermediate species in the present catalytic system. Intramolecular transfer of the α and β-hydrogen would afford aldehydes, $CuFe_2O_4$, and TEMPOH. TEMPOH was oxidized by dioxygen to TEMPO and water.[19b] Further investigations on the more detailed mechanism are ongoing.



Scheme 1 Plausible mechanism

Experimental Section

General experimental procedures

All reagents and solvents were obtained from commercial suppliers and used without further purification. Flash chromatography was performed on silica gel (200 ~ 300 mesh). ^1H and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^1H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.28 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm).

General procedure for synthesis of aldehydes 2a-2n: A 25 mL Schlenk tube was charged with a magnetic stirrer and H_2O (2.0 mL). $CuFe_2O_4$ (0.2 mmol, 47.8 mg), TEMPO (0.25 mmol, 39 mg), and aromatic alcohols (**2**) (2 mmol). The reaction was performed at 100 ℃ for 24 h under dioxygen atmosphere in the sealed tube. After being cooled to room temperature, the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layer was concentrated, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1 to 20:1) to afford the target product (**2a-2n**).

Recycling of the catalyst: After completion of the reaction, the magnetic nanoparticles were recovered by using a Nd-Fe-B based magnet and the organic solvents containing the products collected with a pipet. The recovered catalyst was washed with ethanol and then acetone, and was dried at 120 °C in an oven for 2 h to provide the recycling $CuFe_2O_4$ about 46.2 mg.

Benzaldehyde (2a).[20] Eluent petroleum ether/ethyl acetate (30:1). Yield 95% (201 mg from 216 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 10.0 (s, 1H), 7.87 (d, 2H, J = 8.0 Hz), 7.66 (t, 1H, J = 8.0 Hz), 7.51 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 192.5, 136.4, 134.5, 129.7, 129.0.

4-Chlorobenzaldehyde (2b).[20] Eluent petroleum ether/ethyl acetate (20:1). Yield 79% (221 mg from 284 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.99 (s, 1H), 7.83 (d, 2H, J = 8.0 Hz), 7.52 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 190.8, 140.9, 134.7, 130.9, 129.5.

4-Methoxybenzaldehyde (2c).[20] Eluent petroleum ether/ethyl acetate (25:1). Yield 86% (234 mg from 276 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.89 (s, 1H), 7.84 (d, 2H, J = 8.0 Hz), 7.01 (d, 2H, J = 8.0 Hz), 2.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 190.8, 164.6, 132.0, 130.0, 114.4, 55.6.

4-nitrobenzaldehyde (2d).[20] Eluent petroleum ether/ethyl acetate (30:1). Yield 49% (148 mg from 306 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 10.18 (s, 1H), 8.42 (d, 2H, J = 8.0 Hz), 8.10 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 190.3, 151.2, 140.1, 130.5, 124.3.

4-Methylbenzaldehyde (2e).[20] Eluent petroleum ether/ethyl acetate (30:1). Yield 87% (209 mg from 244 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.96 (s, 1H), 7.82 (d, 2H, J = 8.0 Hz), 7.43 (d, 2H, J = 8.0 Hz), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 193.1, 145.7, 134.5, 130.2, 127.7, 21.9.

4-Bromobenzaldehyde (2f).[20] Eluent petroleum ether/ethyl acetate (30:1). Yield 84% (309 mg from 372 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.97 (s, 1H), 7.54 (d, 2H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 191.0, 135.1, 132.4, 131.0, 129.7.

3,5-Dimethoxybenzaldehyde (2g).[17] Eluent petroleum ether/ethyl acetate (20:1). Yield 94% (315 mg from 336 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.88 (s, 1H), 6.99 (s, 2H), 6.68 (s, 1H), 3.83 (s, 6H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 191.8, 161.2, 138.4, 107.1, 107.0, 55.6.

3-Bromobenzaldehyde (2h).[21] Eluent petroleum ether/ethyl acetate (25:1). Yield 80% (293 mg from 370 mg starting material). ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.99 (s, 1H), 8.04 (s, 1H), 7.84 (d, 1H, J = 8.0 Hz), 7.77 (d, 1H, J = 8.0 Hz), 7.45 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 190.7, 138.0, 137.3, 132.4, 130.6, 128.4, 123.4.

4-(Trifluoromethyl)benzaldehyde (2i). Eluent petroleum ether/ethyl acetate (30:1). Yield 66% (230 mg from 352 mg starting material). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 10.13 (s, 1H), 8.04 (d, 2H, J = 8.0 Hz), 7.84 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 191.1, 138.7, 135.8 (d, J = 26.1 Hz), 131.1, 129.9, 126.1(d, J = 4.1 Hz).

3-Methoxybenzaldehyde (2j).[20] Eluent petroleum ether/ethyl acetate (20:1). Yield 96% (261 mg from 276 mg starting material). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.98 (s, 1H), 7.47-7.45 (m, 2H), 7.40 (s, 1H), 7.20-7.18 (m, 1H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 192.1, 160.2, 137.9, 130.1, 123.5, 121.5, 112.2, 55.5.

3-Phenoxybenzaldehyde (2k). Eluent petroleum ether/ethyl acetate (20:1). Yield 72% (285 mg from 400 mg starting material). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.98 (s, 1H), 7.64-7.61 (m, 2H), 7.54-7.49 (m, 2H), 7.42-7.38 (m, 2H), 7.33-7.29 (m, 1H), 7.20 (t, 1H, J = 8.0 Hz), 7.07 (t, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 191.6, 158.4, 156.2, 138.1, 130.5, 130.1, 124.7, 124.6, 124.2, 119.5, 118.2.

4-Fluorobenzaldehyde (2l). Eluent petroleum ether/ethyl acetate (30:1). Yield 79% (196 mg from 252 mg starting material). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.97 (s, 1H), 7.91 (d, 2H, J = 8.0 Hz), 7.21 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 167.5 (d, J = 10.1 Hz), 132.9, 132.6 (d, J = 26.1 Hz), 116.3(d, J = 3.1 Hz).

Thiophene-2-carbaldehyde (2m). Eluent petroleum ether/ethyl acetate (20:1). Yield 62% (139 mg from 228 mg starting material). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 10.01 (s, 1H), 7.87-7.83 (m, 2H), 7.29 (t, 1H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 183.2, 144.2, 136.2, 135.5, 128.6.

Cinnamaldehyde (2n).[17] Eluent petroleum ether/ethyl acetate (30:1). Yield 85% (224 mg from 268 mg starting material). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.73 (s, 1H), 9.71 (s, 1H), 7.59-7.57 (m, 4H), 7.47-7.44 (m, 6H), 6.75 (d, 1H, J = 8.0 Hz); 6.70 (d, 1H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 200 MHz, ppm) δ 193.7, 152.8, 134.0, 131.3, 129.1, 128.6, 128.5.

Couclusions

In conclusion, We have developed a novel, green and practical magnetic copper ferrite nanoparticle-catalyzed method for aerobic oxidation of primary alcohol to aldehyds. The method is of the following advantages: (a) oxygen-stable and recyclable copper ferrite nanoparticle as the catalyst; (b) environmentally friendly water as the solvent; (c) without addition of any base, ligand or additive; (d) easy workup procedure; (e) outstanding tolerance of functional groups. All these results meet the requirements of green and sustainable chemistry, so the present method will attract much attention in academic and industrial fields. Further studies to catalyze other chemical reaction with copper(II) ferrite magnetic nanoparticles are ongoing.

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