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Efficient synthesis of symmetrical anhydrides by cross dehydrogenative coupling of aryl aldehydes over CuFe₂O₄ nanoparticles

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Abstract

Nano copper ferrite catalyst is prepared and characterized by scanning electron microscopy, energy dispersive X-ray, X-ray diffraction, vibrational sample magnetometry, and Fourier transform infrared. The catalytic activity is probed for cross-dehydrogenative coupling of aromatic aldehydes in the presence of *tert*-butyl hydroperoxide as the oxidant. This catalytic protocol appears as a simple, rather cheap, clean, and efficient practical strategy for the synthesis of symmetrical anhydrides, with proper efficiency (66%). The catalyst can be easily separated from the reaction mixture by an external magnet and reused several times in subsequent reactions, without any measurable loss of its efficiency.

Graphic abstract



Keywords Copper ferrite · Aldehyde · Coupling · Magnetic nanocatalyst · Recyclable

Introduction

Ferrites are ceramic-like materials with magnetic properties which are described by the formula $M(Fe_xO_y)$. Combination of two metals in the oxide matrix and their distribution on octahedral and tetrahedral sites may affect ferrites chemical and physical properties. In general, there are three types of ferrites (spinel ferrite, garnet, and hexagonal ferrite) [1, 2]. Among them, the spinel ferrites are an important class of magnetic nanoparticles where the metallic cations M^{2+} and Fe^{3+} distribution appear on octahedral and tetrahedral sites. Due to their theoretical understanding and potential

Mohamad Z. Kassaee kassaeem@modares.ac.ir applications in science and technology, extensive works on certain spinel ferrites have been carried out [3, 4]. Recently, magnetic nanoparticles have materialized as efficient catalysts because they are recyclable, reusable and stable. In addition, large surface/volume ratio of the nanoparticles is mainly responsible for their catalytic performance. Hence, the catalytic power of the spinel ferrites as a magnetic catalyst has been studied in some chemical reactions [5-7]. In recent years, copper catalysts have received broad interests because of their many advantages such as availability, economy, high activity, high efficiency and low toxicity [8–11]. So, between different spinel ferrites with formula MFe₂O₄ (M=Mn, Fe, Ni, Co, Cu, etc.), CuFe₂O₄ has quite interesting properties and is used for a variety of applications [12–14]. They can be prepared using various methods such as co-precipitation [15], mechano-chemical [16], micelle

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synthesis [17], hydrothermal synthesis [18], etc. Recently, many research groups have explored the vital use of these nano ferrites as green, recyclable, and reusable catalysts in organic synthesis [19–21].

Carboxylic anhydrides are an important class of organic compounds used as versatile reagents in the preparation of carboxylic acid derivatives. They are also employed as a reactive intermediate in various types of reactions [22–25]. Anhydrides are important but less abundant in nature. Therefore, their synthesis is significant for organic chemists. Traditionally, these compounds are prepared by dehydrating carboxylic acids with dehydrating agents such as thionyl chloride [26], phosgene [27], isocyanates [28], carbodiimides [29], phosphoranes [30], and 1,3,5-triazines [31]. Since these procedures are affected by many drawbacks, the development of an improved methodology for the synthesis of anhydrides from easily available starting materials is highly desirable.

In recent years, considerable attention has been attracted to the cross-dehydrogenative coupling (CDC) reactions because of their atom economy, step-economy, and the outstanding role in the formation of C–C and C–X (X = heteroatom) bonds [32, 33]. Aldehydes and other readily available materials are advantageous in CDC reactions [34, 35]. These compounds have been used in significant organic transformations [36–38]. Also, a number of metal catalytic approaches have been developed towards the synthesis of symmetrical anhydrides from aldehydes using *tert*-butyl hydroperoxide (TBHP) as an oxidant [39–41].

Due to copper is a superior activity, in this study we report a novel CDC based approach for the synthesis of symmetrical anhydrides through oxidative activation of sp_2 C–H bond of aldehydes using TBHP as an oxidizing agent and copper ferrite nanoparticles (CuFe₂O₄ NPs) as the catalyst (Scheme 1).

Results and discussion

Here we discuss characterizations of synthesized $CuFe_2O_4$ nanoparticles by various techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and vibrating sample magnetometer (VSM).



In the FT-IR spectrum, two absorption bands corresponding to the stretching vibrations of the tetrahedral and octahedral sites are observed around 600 and 400 cm⁻¹, respectively [42, 43]. The broad absorption band at 3417 cm⁻¹ corresponds to hydroxyl groups stretching vibrations. The peak 1628 cm⁻¹ is due to bendings of H₂O adsorbed at the surface of CuFe₂O₄ (Fig. 1).

The crystalline structure of CuFe_2O_4 is studied via XRD analysis, where all the X-ray diffraction peaks are compared with the standard card (JCPDS NO. 34-0425). Six distinct diffraction peaks can be observed at 21.2°, 35.10°, 41.59°, 50.69°, 63.38°, 67.50° and 74.55° (2 θ), which correspond to the (111), (220), (311), (400), (511), and (440) planes, respectively (Fig. 2). It is revealed that the CuFe₂O₄ nanoparticles have a cubic structure and show the presence of only spinel phase without any impurities.

The SEM image of CuFe_2O_4 shows nanocrystals that have a rod-shaped morphology with a particle size of 70–150 nm and a diameter of about 20–50 nm (Fig. 3). In addition, the energy dispersive X-ray (EDX) analysis shows the presence of Cu, Fe, and O elements in the product (Fig. 4). The ratio of Fe/Cu is very close to their atomic ratio (2:1) in CuFe_2O_4 formula, confirming the formation of nanoparticles.

Magnetic properties of $CuFe_2O_4$ nanoparticles may be estimated by VSM. Its magnetization curves display a saturation magnetization value of 30 emu g⁻¹ (Fig. 5). This shows high permeability in magnetization and high reversibility in the hysteresis loop.

After the preparation and characterization, the catalytic activity of CuFe₂O₄ is explored through the synthesis of symmetrical anhydrides by the CDC of aldehydes. Firstly, to optimize reaction conditions for the formation of benzoic anhydride, the effect of catalyst amount, solvent, oxidant, and reaction temperature are probed. Initial investigation is started in CH₃CN as a solvent, TBHP as oxidant, at different temperatures, and with various amounts of catalyst (Table 1). The results show when the reaction is performed with 1.5 equivalent of TBHP and 20 mg of the catalyst, a maximum yield of 66% is observed in reflux condition in CH₃CN (entry 8). However, with the increasing quantity of TBHP and the catalyst, yield of the product does not improve (entries 9, 10). Furthermore, in the absence of TBHP, no yield for the product is detected (entry 16). The effect of other solvents and oxidants is also tested but the results are ineffective and obtain in lower yields (entries 11-15).

To explore the efficiency and the scope of this protocol, the reaction is evaluated using a range of aromatic aldehydes in optimum conditions (Table 2). Aldehydes having electron-donating groups such as CH_3 and OCH_3 react efficiently to furnish their corresponding anhydrides, under the reaction conditions. For benzaldehydes with methyl group in *ortho* or *para* positions, products **2b** and **2c** are obtained in 61 and 62% yields, respectively. While



Fig. 1 The FT-IR spectrum of CuFe₂O₄ NPs



Fig. 2 The XRD pattern of $CuFe_2O_4$ NPs



Fig. 3 The SEM image of CuFe₂O₄ NPs

p-methoxybenzaldehyde give the corresponding anhydride **2d** with only 56% yield. Likewise, when other aromatic aldehydes bearing more methoxy substituents such as 3,4-dimethoxy- and 3,4,5-trimethoxybenzaldehyde are used, respective anhydrides **2g** and **2h** are detected with modest yields of 44 and 39%, respectively. Then, an aromatic aldehyde possessing electron-withdrawing group such as *p*-chlorobenzaldehyde is reacted and converted to the corresponding product **2e** in 34% yield. Moreover,

intramolecular CDC of an aromatic *o*-phthaldehyde leads to the formation of phthalic anhydride **2f** in 52% yield.

For the synthesis of symmetric anhydrides with this methodology, a plausible mechanism is suggested (Scheme 2). Initially, *t*-butyloxy radical is generated by conversion of the copper(II) to copper(III) species through electron transfer to TBHP. Then, the *t*-butoxyl radical abstracts a hydrogen atom from the aldehyde which leads to the formation of an acyl radical. Next, the acyl radical couples with *t*-butylperoxy radical, affording a perester intermediate. The cleavage of the O–O bond in this intermediate generates the carboxyl radical which combines with another acyl radical giving the desired anhydride [39, 41].

The recovery and reuse of catalysts are desirable for a greener process. Hence, the reusability of the catalyst is investigated for our model reaction. The catalyst is magnetically recovered by an external magnetic field and washed with EtOH. After being dried, it is reused in the next run. The procedure is repeated and the results indicate that the catalyst could be recycled three times without a significant loss of its activity (Fig. 6).

Comparison of catalytic efficiency of $CuFe_2O_4$ NPs with those reported in the literature, for the synthesis of anhydrides from aldehydes, indicates that our method is simpler, more convenient with the easier operation, and with the reusability of the nanocatalyst in several catalytic cycles (Scheme 3) [39, 41].



Energy / keV



Fig. 5 The VSM curve for CuFe₂O₄ NPs

Table 1 Screening of the reaction conditions for synthesis of benzoic anhydride (2a) from benzaldehyde over $CuFe_2O_4$

Entry	Catalyst/mg	Solvent	Oxidant (equiv.)	Temp./°C	Yield ^a /%
1	10	CH ₃ CN	TBHP (1.5)	25	_
2	10	CH ₃ CN	TBHP (1.5)	50	10
3	10	CH ₃ CN	TBHP (1.5)	Reflux	28
4	15	CH ₃ CN	TBHP (1.5)	Reflux	37
5	15	CH ₃ CN	TBHP (1)	Reflux	22
6	15	CH ₃ CN	TBHP (2.5)	Reflux	32
8	20	CH ₃ CN	TBHP (1.5)	Reflux	66
9	25	CH ₃ CN	TBHP (1.5)	Reflux	68
10	20	CH ₃ CN	TBHP (2.5)	Reflux	50
11	20	CH_2Cl_2	TBHP (1.5)	Reflux	<10
12	20	Dioxane	TBHP (1.5)	Reflux	23
13	20	Toluene	TBHP (1.5)	Reflux	27
14	20	CH ₃ CN	H_2O_2	Reflux	<5
15	20	CH ₃ CN	NaOCl	Reflux	_
16	20	CH ₃ CN	-	Reflux	-

^aIsolated yield

Conclusion

In continuation of our research, a heterogeneous nanocatalyst, $CuFe_2O_4$ NPs, was fabricated and characterized. Subsequently, it was employed in an efficient preparation of symmetrical anhydride derivatives. This achievement was reached through the treatment of substituted aromatic aldehydes over the magnetically separable $CuFe_2O_4$ NPs with easy handling, simple workup procedure, ease of separation, and recyclability of the catalyst. The magnetic nanocatalyst was stable and could be reused in three successive runs with no significant structural change or loss of activity.

Experimental

All chemical reagents used in our experiments are purchased from Merck or Aldrich Chemical Company with high purity. All solvents are distilled, dried and purified using standard procedures. Thin-layer chromatography (TLC) is performed using aluminium plates coated with silica gel 60 F-254 (Merck). Melting points are measured on an Electrothermal 9100 apparatus. Fourier transform infrared (FT-IR) spectra are recorded using KBr pellets on a Nicolet IR-100 infrared spectrometer. The powder X-ray diffraction spectrum is recorded at room temperature using a Philips X-Pert 1710 diffractometer with Co K α (α = 1.79285 Å) voltage of 40 kV, current of 40 mA, in the range of 20° – 80° (2 θ) with a scan speed of 0.02°/s. An energy-dispersive detector (EDS) coupled to the microscope is used to identify chemical elements of the prepared catalyst. The particle morphology is examined by scanning electron microscopy using SEM (HITACHI S-4160). Magnetic properties are obtained by a vibrating magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran).

General procedure for the synthesis of CuFe₂O₄ NPs

The CuFe₂O₄ nanoparticles are prepared through a coprecipitation method [21, 45, 46]. In a typical procedure, the required amount of Cu(NO₃)₂•3H₂O (0.5 g, 2.05 mmol) and Fe(NO₃)₃•9H₂O (1.67 g, 4.1 mmol) are dissolved, then NaOH solution (2 M) is added dropwise at room temperature until a reddish-black precipitate is formed. Then, the temperature is raised to 90 °C and stirring is done for 6 h. The resulting precipitate is separated by a magnetic separator, washed with deionized water for several times and dried at 80 °C overnight. Finally, the powder is calcined in a furnace at 500 °C for 5 h.

Comp	Structure	Yield/%	M.p./°C	Lit. m.p./°C
2a		66	_	Colorless oil [39, 41]
2b		61	-	Liquid [41]
2c	H-C CH	62	83–85	83–86 [39, 41]
2d		56	95–97	95.5–97.5 [39, 41]
2e		34	179–181	180–182 [44]
2f		52	130–132	132–134 [39, 41]
2g		44	123–125	122–124 [40, 41]
2h	H_3CO H_3CO H_3CO OCH_3 OCH_3 OCH_3 OCH_3	39	157–159	158–160 [39, 40]

Table 2 Substrate scope for synthesis of anhydrides from aldehydes over CuFe₂O₄

Reaction conditions: arylaldehyde (1 mmol), TBHP (1.5 equiv), 2 cm³ CH₃CN, 20 mg CuFe₂O₄, 80 °C, 4 h. Isolated yield

General procedure for the synthesis of aromatic anhydrides over CuFe₂O₄ catalyst

A solution of aldehyde (1 mmol) and $CuFe_2O_4$ (20 mg) in 2 cm³ CH₃CN, TBHP (1.5 eq. from a 6 M solution of in decane) is slowly stirred. Then, the reaction mixture is refluxed for the appropriate time (the reaction progress was monitored by TLC). After completion of the reaction, the solvent is evaporated and the residue is extracted with ethyl acetate and 10% saturated NaHCO₃ solution. The organic layer is then dried with anhydrous sodium sulfate. The crude product is purified using silica gel column chromatography (hexane/ethyl acetate (8:2) to give the desired anhydride.







Fig. 6 Reusability of CuFe₂O₄ NPs in the model reaction



Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00706-021-02741-7.

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