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Nano CuFe$_2$O$_4$: An efficient, magnetically separable catalyst for transesterification of β-ketoesters.

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The preparation of a variety of β-ketoesters was achieved in high yields from methyl acetoacetate under neutral conditions through the utilization of magnetic CuFe$_2$O$_4$ nanoparticles as catalyst. Recycling of the catalyst was performed up to eight times without significant loss in activity. The catalyst was characterized using XRD, XPS, SEM and TEM techniques.

Introduction

β-Ketoesters are important synthons prepared by reacting highly reactive and unstable diketenes with various alcohols.[1] They can be transformed into chiral building blocks by chemical and enzymatic transformation and functions as a tool to perform chain-extension reactions.[2]

Transesterification is one of the most effective methods for the preparation of esters and thus possess wide application in both academic and industrial research.[3] This transformation can be accelerated by protic[4] and Lewis acids[5] as well as alkaline catalysis.[6] Among the variety of catalysts[7] effecting transesterification, DMAP,[8] tetrabutyldistannoxane,[9] NBS,[10] Ag(OTf)[11] and Yb(OTf)$_3$[12] represent a few homogeneous examples. Some of the drawbacks of homogeneous transesterification are troublesome isolation of the product, catalysts not always recyclable and large volumes of undesirable waste generated during workup. Furthermore, selectivity is often low resulting in unwanted mixtures of products.

The majority of protic acid catalysts are highly corrosive and, hence, not ecofriendly which lead to the development of various heterogeneous analogues for the transesterification of methyl and ethyl acetoacetates in particular. Examples of acidic heterogeneous catalysts for the transesterification of β-ketoesters include, among others,[13] zeolites,[14] kaolinic clay[15] and yttria-zirconia.[16] A recent report by Romanski et al.[17] claim the transesterification of sterically hindered esters under elevated pressures which requires special equipment and precautions to perform safely.

Magnetic nanoparticles have recently emerged as a useful group of heterogeneous catalysts finding numerous applications in synthesis and catalysis.[18] The separation of magnetic nanoparticles is simple and economical which represents an attractive alternative to filtration or centrifugation. Magnetic separation diminishes the loss of catalyst resulting in enhanced reusability making these catalysts cost-effective and promising for industrial applications. In addition, they exhibit high catalytic activity due to their large surface area, relatively low preparation costs as well as low toxicity making them highly desirable and promising catalysts.[19] Super magnetic copper ferrite, CuFe$_2$O$_4$, is an example of a catalyst which has demonstrated application in various organic transformations.[20] The efficacy of CuFe$_2$O$_4$ motivated the current study. Herein we report, for the first time, the utilization of CuFe$_2$O$_4$ as magnetic heterogeneous catalyst for the effective transesterification of β-ketoesters with various alcohols to produce versatile, diversified esters in moderate to excellent yields.

Experimental

General

The crystalline structure of the CuFe$_2$O$_4$ was analyzed using a Bruker D8 Advance powder diffractometer (XRD; X-ray diffraction). The x-ray photoelectron spectroscopic (XPS) analysis of CuFe$_2$O$_4$ was carried out with a PHI 5000 Versaprobe Scanning ESCA Microprobe, while scanning electron microscopy (SEM) images were obtained on a Shimadzu SSX-550 Superscan scanning electron microscope. Transmission electron microscopy (TEM) images were obtained on a Philips (FEI, The Netherlands) CM100 transmission electron microscope. Nuclear magnetic resonance (NMR) spectra for ^{1}H (600 MHz) and ^{13}C (150 MHz) were recorded on a Bruker AM-600 FT spectrometer using CDCl$_3$ as solvent with tetramethylsilane (TMS) as the internal reference. Gas-chromatography mass-spectrometry (GCMS) was performed on a Shimadzu GCMS-QP2010 instrument.

Catalyst preparation

A mixture of $Cu(OAc)_2$ (0.91 g, 5 mmol) and $Fe(NO_3)_3\cdot 9H_2O$ (4.04 g, 10 mmol, 2 eq.) was dissolved in an aqueous 0.1 M NaOH (50 ml) solution and heated to 90 °C with mild stirring for 2 hours. The black precipitate was filtered off, washed with ethanol (3 × 50 ml) and water (50 ml) and annealed at 650 °C for 1 hour in air to yield $CuFe_2O_4$ as magnetic nanoparticles.[21,22]

Catalyst characterization

XRD spectrum of $CuFe_2O_4$ is presented in Figure 1 (a). All the diffraction peaks in the XRD pattern can be indexed to those of the tetragonal structure of copper ferrite $CuFe_2O_4$ according to JCPDS file No. 35-0425 and is in agreement with the reported spectra.[22] The XPS survey of $CuFe_2O_4$ nanoparticles is shown in to Figure 1 (b) which reveals only copper, iron, and oxygen core levels.
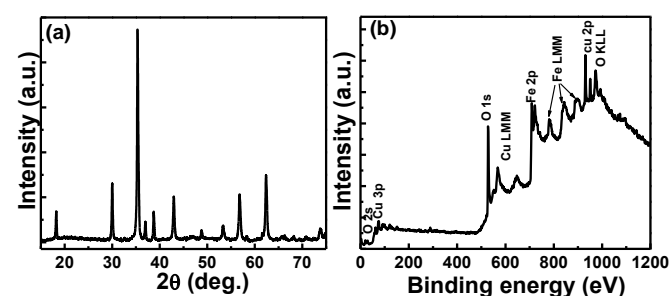

Figure 1: (a) XRD spectra and (b) XPS survey spectrum of $CuFe_2O_4$ nanoparticles.

The crystallite size (D) of $CuFe_2O_4$ is calculated using Scherer's formula[23] given below

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where, λ is the wavelength of Cuk_α radiation (0.1514 nm), K is correlation factor (0.94), β is FWHM (full width at half maximum) of peaks and θ is Bragg's diffraction angle. Crystallite size of the $CuFe_2O_4$ nanoparticles was observed to be *ca*. 50 nm according to the TEM image [Figure 2 (a)]. The SEM micrographs for $CuFe_2O_4$ [Figure 2 (c)] with a 10 μm field of view displays the very fine and homogenous nanosphere particles containing some degree of agglomeration. The observed morphology is the same as what has been reported in the literature for $CuFe_2O_4$.[22] The agglomeration of particles can be related to many factors such as shape factor, surface area, porosity, and density.[24] The TEM [Figure 2 (b)] and SEM [Figure 2 (d)] images of $CuFe_2O_4$ nanoparticles recovered after several cycles of transesterification reactions reveal similar characteristics.

General method for transesterification

A mixture of methyl acetoacetate (**1**) (2.0 mmol), the corresponding alcohol (**2**) (2.1 mmol) and $CuFe_2O_4$ catalyst (10 mol%) in toluene (10 mL) was heated to reflux. Upon completion of the reaction (assessment by TLC), the catalyst was immobilized by employing an external magnet and washed with ethyl acetate. The organic solution was dried over

anhydrous Na_2SO_4 and the solvent removed under reduced pressure. Purification of the crude product was achieved through column chromatography on silica gel by utilizing *n*-hexane-ethyl acetate (10:1) as eluent to afford the pure β-ketoester (**3**). The isolated product was then subjected to ^{1}H NMR, ^{13}C NMR and GCMS analysis for structural confirmation.
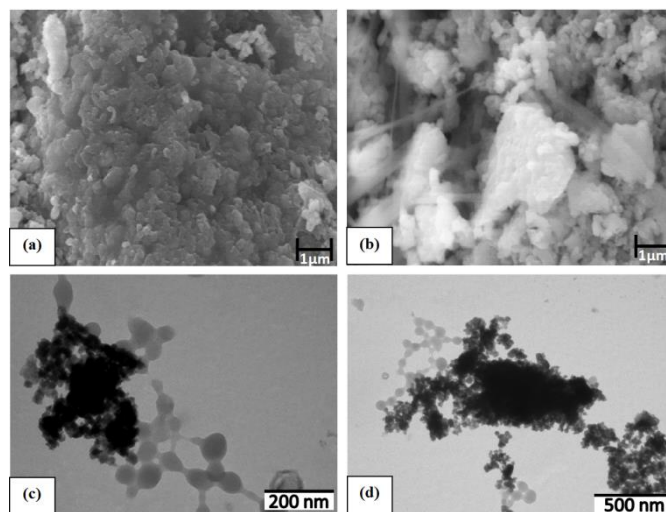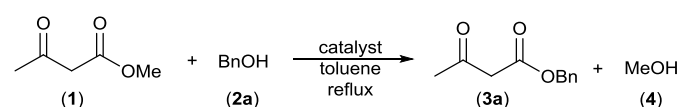

Figure 2: TEM image of (a) fresh $CuFe_2O_4$ and (b) spent $CuFe_2O_4$ nanoparticles. SEM images of (c) fresh $CuFe_2O_4$ and (d) spent $CuFe_2O_4$ nanoparticles.

Results and discussion

The reaction conditions (reflux, 6 hours) was established with a mixture of methyl acetoacetate (**1**) (2 mmol), benzyl alcohol (**2a**) (2.1 mmol) and $CuFe_2O_4$ in toluene (10 mL) (Scheme 1).

Scheme 1: Transesterification of methyl acetoacetate (**1**) with benzyl alcohol (**2a**) to produce benzyl acetoacetate (**3a**).

The catalyst loading of $CuFe_2O_4$ was evaluated and 10 mol% (Table 1; entry 1) was identified as the optimal loading as it was superior to 5 mol% (entry 8) and yielded comparable results to 15 mol% (entry 9). Several other nano-magnetic catalysts like Fe_3O_4, Fe_2O_3, $NiFe_2O_4$, $CoFe_2O_3$ and $MoFe_2O_3$ were also compared to $CuFe_2O_4$ (entries 2-7) and it was found that although similar product yields were obtained for these catalysts, $CuFe_2O_4$ required shorter reaction times (6 hours vs. 8 hours). The $CuFe_2O_3$ catalyst was also compared to other widely used non-magnetic heterogeneous catalysts like ZnO, CuO, Al_2O_3 and V_2O_5 and found to be superior also to these compounds with higher yield being obtained after the same reaction time (entries 11-14).

Due to the affinity of copper for oxygen, the transesterification reaction could be envisaged as the result of

the Cu center in the catalyst forming a bi-dentate complex (**A**) with the substrate (**1**). This would render a more electrophilic ester moiety that could be attacked by the alcohol nucleophile giving the tetrahedral intermediate (**B**) and subsequent hydrogen transfer (**C**) to liberate methanol and the product ester **3**.[25] Continuous removal of the low boiling alcohol (methanol) at the elevated temperature would then shift the equilibrium toward the desired β-ketoester (**3**).

Table 1: Optimization of transesterification reaction conditions with methyl acetoacetate (**1**) and benzyl alcohol (**2a**).[a]

Entry	Catalyst	Time (h)	Yield (3a)[b] (%)
1	$CuFe_2O_4$	6	94
2	$CoFe_2O_4$	8	92
3	$MoFe_2O_4$	8	93
4	$NiFe_2O_4$	8	92
5	$ZnFe_2O_4$	8	92
6	Fe_2O_3	8	92
7	Fe_3O_4	8	92
8	$CuFe_2O_4$ (5 mol%)	6	80
9	$CuFe_2O_4$ (15 mol%)	6	93
11	ZnO	6	80
12	CuO	6	70
13	Al_2O_3	6	75
14	V_2O_5	6	88

[a]*Conditions:* **1** (2 mmol), **2a** (2.1 mmol) and catalyst (10 mol%) in refluxing toluene (10 mL). [b]Isolated yield.
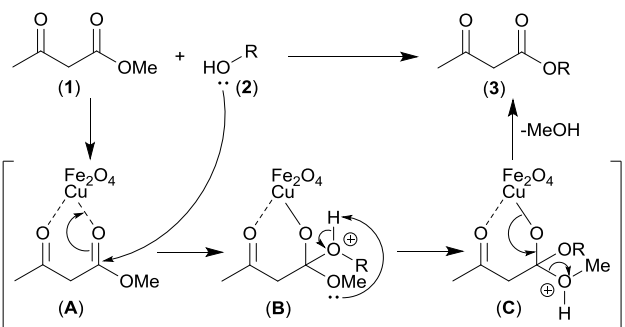
Scheme 2: Proposed $CuFe_2O_4$ catalyzed mechanism for the transesterification of methyl acetoacetate (**1**).

The scope of the reaction was evaluated next by employing a variety of alcoholic substrates (Table 2). Substituents on the benzyl alcohol substrates included an electron-withdrawing nitro group (entry 2) and electron-donating methoxy substituents (entries 3-5). Although similar product yields could be achieved, the less nucleophilic nitro containing benzyl alcohol required an additional 2 hours of reaction time for the reaction to go to completion. Of particular importance is the product selectivity obtained for 2- and 4-methoxybenzylalcohol (entries 3 and 5). Despite the tendency of these substrates to undergo dehydroxylation to benzylic carbocations (as a result of benzoquinone formation),[24] no carbon-carbon bond formation to the α-carbon of the ketoester (**1**) was observed and only the transesterified β-ketoesters (**3c**) and (**3e**) were obtained as products.

Other nucleophilic substrates subjected to these conditions include 2-thiophenyl-methanol and 2-furanyl-methanol (entries 6 and 7), which gave their respective β-ketoester in *ca.* 80% yield. Aliphatic alcohols were also highly effective and produce the corresponding β-ketoesters in excellent yields (entries 14-17). A drop in yield to 80% was, however, observed for the sterically more hindered 2-butanol analogue (entry 13). Allylic alcohols (entries 8 and 12) were also very effective (85 and 90%) with propargyl alcohol (entry 9) and crotyl alcohol (entry 10) producing the lowest yields at *ca.* 70%. Since the latter alcohols (**3i** and **3j**) are notorious with respect to instability towards acid catalysts, the low yields obtained for these substrates are probably explicable in terms of polymerization, atmospheric oxidation and/or other side reactions.

Table 2: Transesterification of methyl acetoacetate (**1**) with various alcohols.[a]

Entry	R	Product[b]	Time (h)	Yield[c] (%)
1	$C_6H_5-CH_2$	(**3a**)[26]	6	94
2	$4-NO_2-C_6H_4-CH_2$	(**3b**)[27]	8	90
3	$4-OCH_3-C_6H_4-CH_2$	(**3c**)[26]	6	91
4	$3-OCH_3-C_6H_4-CH_2$	(**3d**)[28]	6	91
5	$2-OCH_3-C_6H_4-CH_2$	(**3e**)[28]	6	84
6		(**3f**)[28]	6	80
7		(**3g**)[26]	6	78
8		(**3h**)[26]	8	85
9		(**3i**)[29]	8	70
10		(**3j**)[26]	8	67
11		(**3k**)[26]	8	90
12		(**3l**)[30]	8	90
13		(**3m**)[30]	8	80
14	C_5H_{11}	(**3n**)[31]	8	95
15	C_6H_{13}	(**3o**)[32]	8	94
16	C_7H_{15}	(**3p**)[32]	8	92
17	C_8H_{17}	(**3q**)[29]	8	90

[a]*Conditions:* **1** (2 mmol), **2** (2.1 mmol) and $CuFe_2O_4$ (10 mol%) in refluxing toluene (10 ml). [b]Structures where confirmed by comparing ^{1}H NMR spectra to reported data. [c]Isolated yields.

Reusability of catalyst

An important aspect for heterogeneous catalysis is simple recovery and reusability of the catalyst. The reusability of $CuFe_2O_4$ was tested on the model reaction between methyl acetoacetate (**1**) and benzyl alcohol (**2a**) [Scheme 1 and Figure 3 (a)]. Upon completion of the reaction, the catalyst was retained with an external magnet [Figure 3 (b)], while the reaction mixture was decanted. In order to remove residual product, the catalyst was washed with ethyl acetate, dried under vacuum and utilized in a repeat reaction.

Following this procedure the catalyst was successfully recycled 8 times reflecting comparable results for all repetitions (Table 3). These results suggest that $CuFe_2O_4$ is a highly stable and effective catalyst for the transesterification of methyl acetoacetate to produce various β-ketoesters.
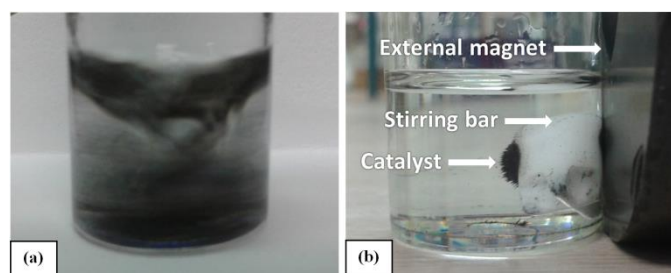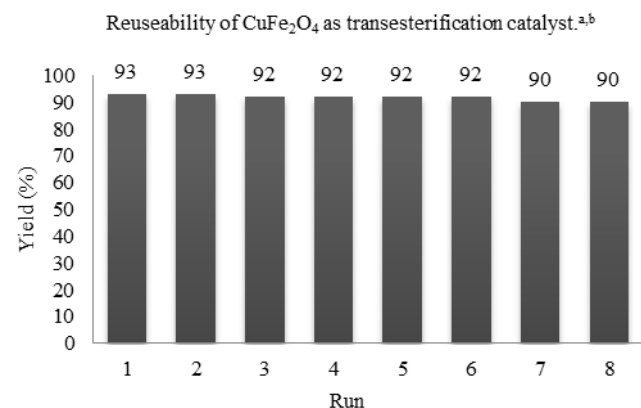

Figure 3: (a) The suspended $CuFe_2O_4$ particles during reaction and (b) the magnetic separation/immobilization of the catalyst upon completion of the reaction.

Graph 1: Recycling of $CuFe_2O_4$ catalyst for transesterification reaction. [a]*Conditions:* **1** (2 mmol), **2a** (2.1 mmol) and $CuFe_2O_4$ (10 mol%) in refluxing toluene (10 mL) for 6 h. [b]Isolated yield.

Conclusion

In conclusion, magnetic $CuFe_2O_4$ nanoparticles are proven, for the first time, as an effective and selective catalyst for the transesterification of methyl acetoacetate to produce a variety of β-ketoesters **3**. In addition to high selectivity, the ease of separation and high stability of $CuFe_2O_4$ makes these nanoparticles highly attractive as a transesterification catalyst.

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