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Synthesis of a Novel Nanomagnetic Catalyst Based on Iron Oxide Nanoparticles for New Oxidative C-O Cross-Coupling Reactions

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Abstract

Vinyl benzoate compounds and enol carbamate derivatives are synthesized through coupling reactions and in the presence of a new nanomagnetic catalyst based on iron oxide nanoparticles. The novel nanomagnetic catalyst consisting of a copper (II) complex on silica-coated iron oxide nanoparticles ($Fe_3O_4.SiO_2$) with good features and high performance. Both types of reactions were well performed by using a new nanomagnetic catalyst. In the first series of reactions, the reaction of beta-dicarbonyl compounds and an alkylbenzene such as toluene as reactants were used, and in the second series of reactions, beta-dicarbonyl compounds with N, N-Dimethylformamide (DMF) were used as reactive substances. The results showed that in the presence of the nanocatalyst, the products were well synthesized.

Keywords:* *Coupling reactions; Vinyl benzoate; Enol Carbamate; Nanocatalyst; Iron oxide

Introduction

The formation of Carbon-Hydrogen bonds to Carbon-Oxygen bonds *via* coupling reactions is a good procedure for the preparation of various compounds that are of chemical, pharmaceutical, and industrial interest [1]. The use of copper salts to perform coupling reactions is an old and time-consuming method among chemical reactions [2]. Nanoparticles of iron oxide (Fe_3O_4) are used to make new catalysts. In this method, to prevent oxidation of iron, nanoparticles of silicon coat on iron ($Fe_3O_4.SiO_2$) and then the other reactions are performed [3]. Iron oxide magnetic nanoparticles have turned out to be very attractive in recent years as readily available and inexpensive Nanocatalysts. The magnetic nanoparticles can easily be retrieved from the reaction mixture and reused by simple magnetic separation and, more importantly, surface repair of these nanomaterials makes it possible to suit their reactivity and to design catalysts for special purposes [4]. Iron catalysts play an important role in organic synthesis because they are relatively safe and stable when compared to other transition metal catalysts. In recent years, transition metal-catalyzed C−H functionalization has been developed as an attractive and powerful strategy as this method permits a more efficient synthesis of functionalized molecules by minimizing the number of synthetic steps [5]. Metal catalyzed coupling reactions have become an important tool in organic chemistry for C-C and C-X bond formations. A lot of compounds, drugs, and complex natural products have successfully built utilizing these reactions [6]. One of the problems with the use of homogeneous catalysts is the difficult separation and contamination of the products. The problems that have been involved are very important in big-scale industrial and environmental projects. It seems that the use

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of heterogeneous nano-catalysts is a good solution to these problems [7]. The important tip is that heterogeneous nano-catalysts can easily be separated without diminishing their catalytic properties [8,9]. The ability to separate catalysts by filtration or centrifugation is very vital because it also prevents the catalyst from being lost and increases the purity of the products, all of which emphasizing the importance of synthesis and the use of these types of nanocatalysts [10,11]. It can be said, the use of the new nanocatalyst be instrumental in improving synthetic reactions. Various studies have been devoted to the properties which affect the catalytic selectivity and activity of nanocatalysts. In recent years, scientists have successfully used Magnetic Nanoparticles [12,13] (MNPs) for the synthesis of new catalysts. As an example, MacMillan catalyst onto slightly cross-linked [14] Merrifield resin and superparamagnetic Iron Oxide (Fe3O4) nanoparticles using of the Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) reactions and the use of the resulting species as recoverable nanocatalysts for the Friedel Crafts Acylation (F-C) of N-substituted pyrroles with α,β-unsaturated aldehydes by using carbene catalysts [16]. Also, synthesis vinyl benzoate compounds can be obtained vinyl benzoate polymers (Polyvinyl Benzoate), which used in drug delivery and molecular delivery as carrier polymers. It has been reported, that these nanoparticles can be useful in the treatment of diseases and also are stable in phosphate buffer and blood serum, and only slowly degrade in the presence of esterases.

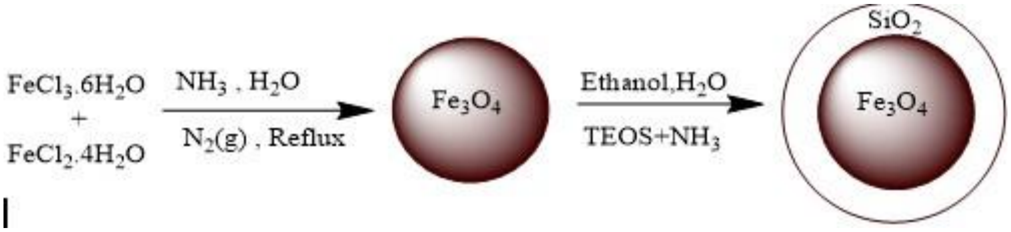
Materials and Methods

All chemicals and reagents were provided from Merck, Sigma-Aldrich, and Carl Roth, also all types of glassware were purchased from Isolab. Identification of the new magnetic nanocatalyst was done using FT-IR, XRD, EDX, VSM, and SEM analyzes and molecular structure. The use of magnetic nanocatalysts in the new method will lead to saving time and temperature of the reaction in a way that reaction is completed in much less time with an efficiency of more than 95%. The identification of products was also done with high accuracy by using IR and HNMR spectroscopies.

Results and Discussion

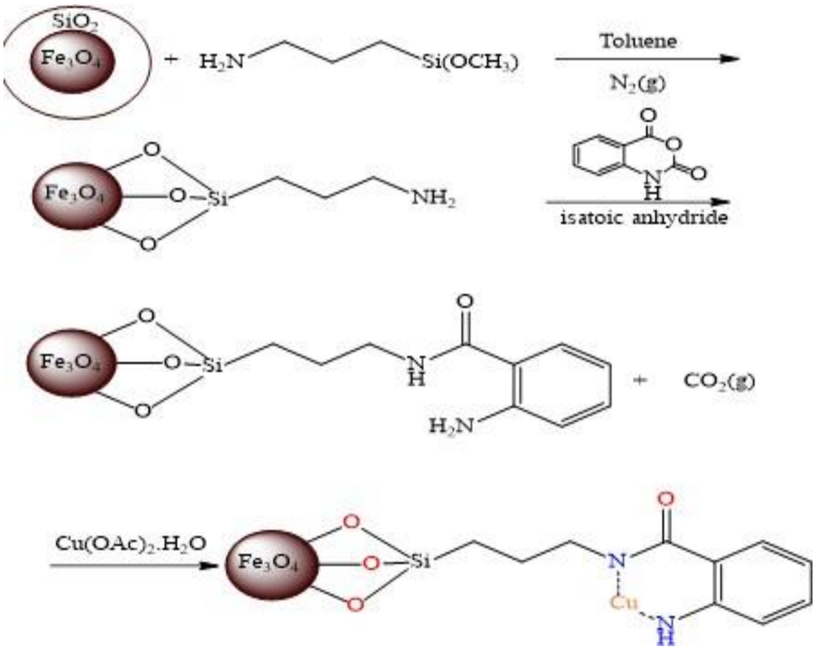
At first, we used copper (II) acetate powder to perform these reactions. Mixing 1 mmol ethyl acetoacetate and 5mmol of toluene. Then, 2 mmol T-Butyl Hydro Peroxide (TBHP) as an oxidant and 0.2 mmol of copper (II) acetate were added to the mixture. This reaction was done at 120℃ for about 6 hours, which gave a vinyl benzoate compound and in the next steps, five other beta-dicarbonyls (methyl acetoacetate, acetylacetone, benzyl acetoacetate, isopropyl acetoacetate, and t-butyl acetoacetate) were reacted with toluene in similar conditions that obtained five different products.

After performing the initial reactions, we attempted to synthesize a new catalyst. Initially, silica-coated iron nanoparticles ($Fe_3O_4.SiO_2$) were prepared from $FeCl_3$, $FeCl_2$, and Tetraethyl Orthosilicate (TEOS) **(SCHEME 1)**.



SCHEME 1. **Silica Coating on the Iron (III) Oxide.**

Then, by adding an equal amount of ($Fe_3O_4.SiO_2$) and 3-Aminopropyl 3-Methoxy Silane (APTMS) using 30 ml of toluene as a solvent, the reaction was refluxed at 111°C for 12 hours. After the first step, the reaction mixture was washed with ethanol and after being dried, isotonic anhydride (1.09 gm) and toluene (50 ml) were added to nanoparticles and the reflux was done again. In the final step, 1.2 gm of copper acetate and 50 ml of methanol were added to the mixture and then refluxed at 64℃ for 12 hours. Finally, the magnetic nanocatalyst was synthesized **(SCHEME 2).**



SCHEME 2. **Synthesis of the new Nanomagnetic Catalyst.**

Images taken by electron microscopy show that these nanoparticles are powder-shaped, and are synthesized in sizes less than 100 nanometers. It should be noted that the magnification of these images (SEM) is 40 Kx bigger with nanoparticles being spherical and porous **FIG. 1**.

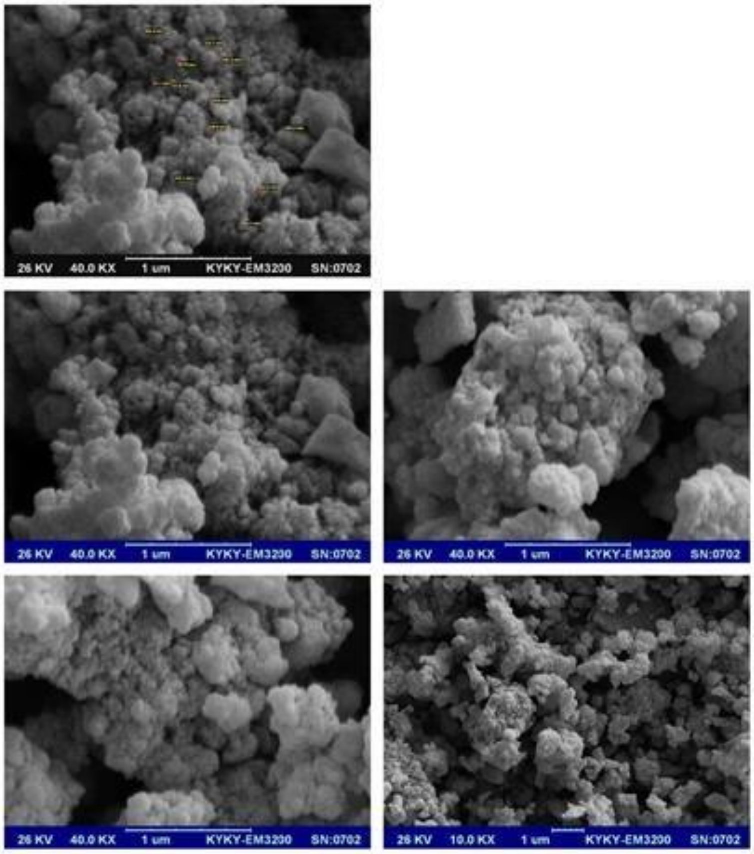


FIG. 1. **Scanning electron microscopy of new magnetic nanocatalyst (SEM).**

Energy-Dispersive X-Ray Spectroscopy (EDX) shows that our magnetic nanocatalyst includes Carbon, Nitrogen, Oxygen, Iron, Copper, and Silicon elements **FIG. 2**, Also since the quantum fields are very small and complex in the nanoparticles, these particles have superparamagnetic properties **FIG. 3.**

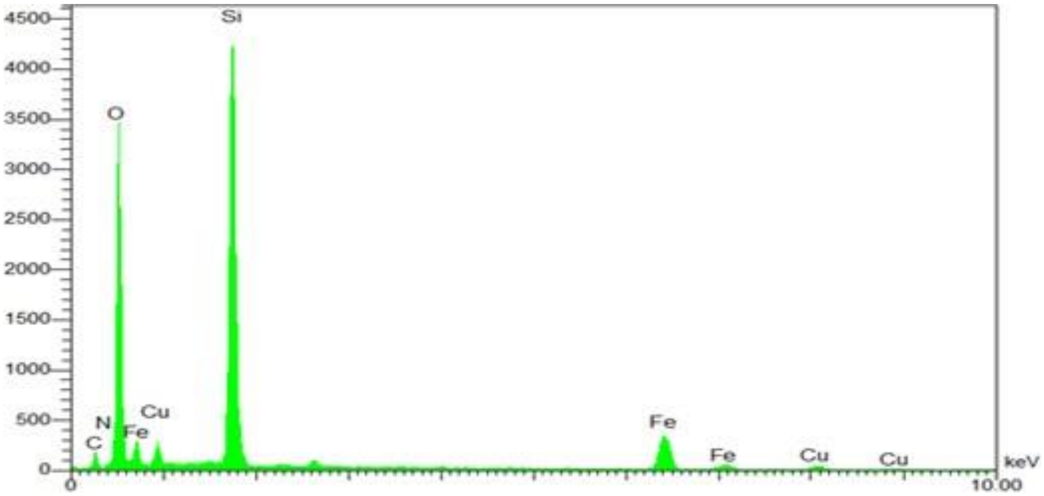


FIG. 2. **Energy-Dispersive X-ray (EDX) spectroscopy of magnetic nanocatalyst.**

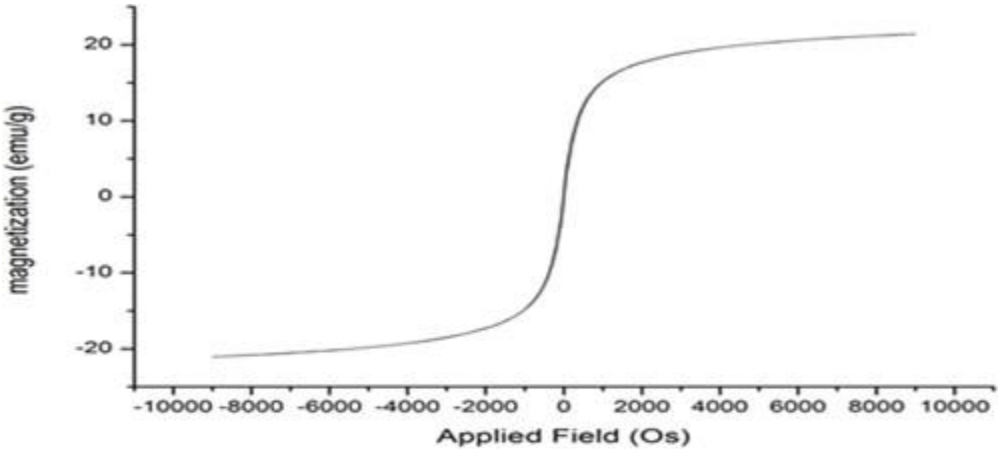
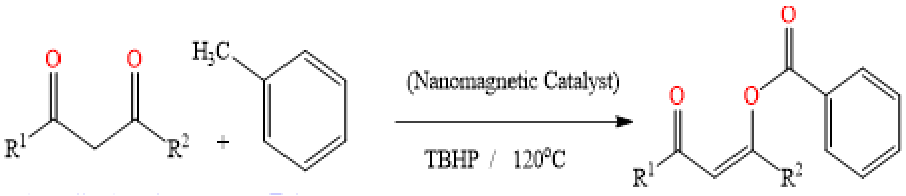


FIG. 3. **Vibration sample magnetometry of magnetic nanocatalyst (VSM).**

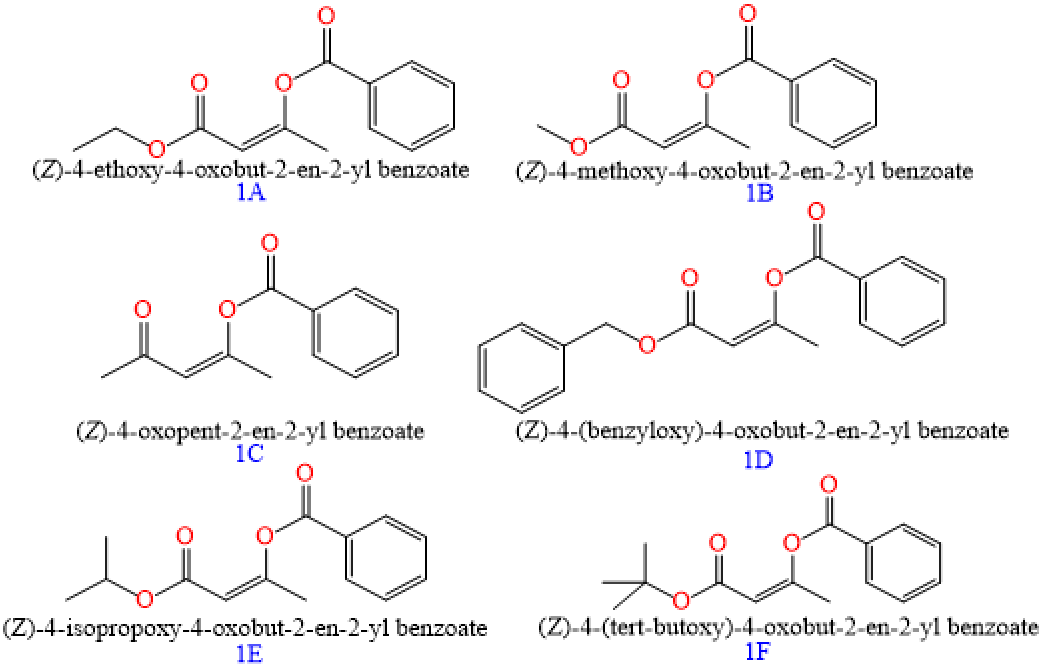
We examined this reaction with the new nanomagnetic catalyst, instead of copper acetate, as a new catalyst **(SCHEME 3)**. We mixed 1 mmol beta dicarbonyl compounds and 5 mmol of toluene. Then, 2 mmol T-Butyl Hydroperoxide (TBHP) as an oxidant and 10 mg of nanomagnetic catalyst were added to the mixture. This reaction was performed at 120°C for about 1 hour, which gave us six new products **TABLE 1**.



SCHEME 3. **Synthesis of vinyl benzoate by using a new Catalyst.**

TABLE 1. **Synthesis of vinyl benzoate compounds in the presence of new Catalyst.**

Entry	R^1	R^2	Product	Time(h)	Yield%
1	O-Et	Me	1A	1	92
2	O-Me	Me	1B	1	90
3	Me	Me	1C	1	80
4	O-Bn	Me	1D	1	85
5	O-iPr	Me	1E	1	80
6	O-tBu	Me	1F	1	78


(Z)-4-ethoxy-4-oxobut-2-en-2-yl benzoate
1A

(Z)-4-methoxy-4-oxobut-2-en-2-yl benzoate
1B

(Z)-4-oxopent-2-en-2-yl benzoate
1C

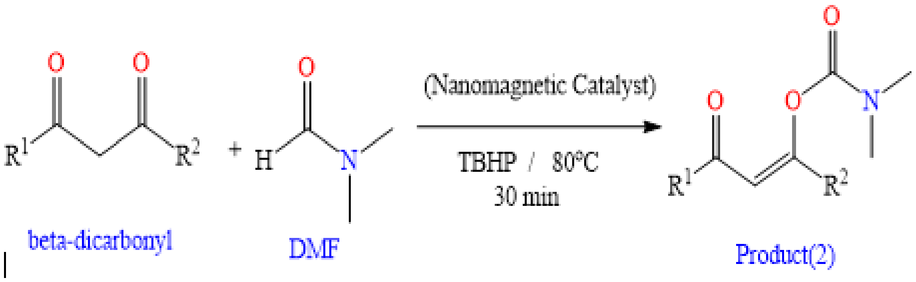
(Z)-4-(benzyloxy)-4-oxobut-2-en-2-yl benzoate
1D

(Z)-4-isopropoxy-4-oxobut-2-en-2-yl benzoate
1E

(Z)-4-(tert-butoxy)-4-oxobut-2-en-2-yl benzoate
1F

SCHEME 4. **Synthesis of vinyl benzoate compounds in the presence of new Catalyst.**

Consequently, we made six new reactions with this catalyst. Following that, we examined the reaction of six beta-dicarbonyls with N, N-Dimethylformamide in the presence of the magnetic nanocatalyst with T-Butyl Hydroperoxide (TBHP) as an oxidant **(SCHEME 4, SCHEME 5**). Optimal results were obtained for the reaction in the presence of 10 mg nanomagnetic catalyst and 2 mmol T-Butyl Hydroperoxide (TBHP) at 80℃ for a half-hour, which gave a 90% yield of ethyl (Z)-3-((dimethyl carbamoyl)oxy)but-2-enoate(2A), 92% yield of methyl (Z)-3-((dimethyl carbamoyl)oxy)but-2-enoate(2B), 78% yield of (Z)-4-oxopent-2-en-2-yl dimethyl carbamate(2C), 87% yield of benzyl (Z)-3-((dimethyl carbamoyl)oxy)but-2-enoate(2D), 78% yield of isopropyl (Z)-3-((dimethyl carbamoyl)oxy)but-2-enoate(2E) and 75% yield of t-butyl (Z)-3-((dimethyl carbamoyl)oxy)but-2-enoate(2F) that gave us six new derivatives **(SCHEME 6), TABLE 2**.



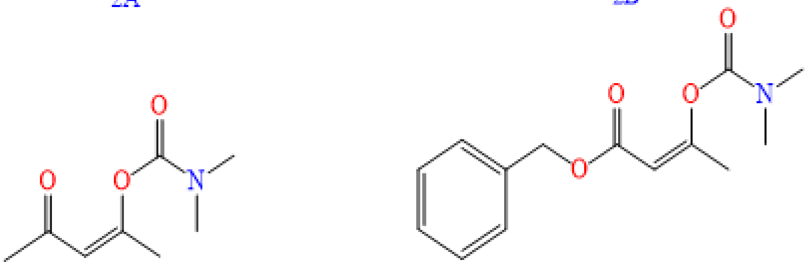
SCHEME 5: **Synthesis of enol carbamate derivatives by using a new Catalyst.**

TABLE 2. **Synthesis of enol Carbamate derivatives in the presence of a new Catalyst.**

Entry	R^1	R^2	Product	Time(h)	Yield%
1	O-Et	Me	2A	0.5	90
2	O-Me	Me	2B	0.5	92
3	Me	Me	2C	0.5	78
4	O-Bn	Me	2D	0.5	87
5	O-iPr	Me	2E	0.5	78
6	O-tBu	Me	2F	0.5	75

ethyl (*Z*)-3-((dimethylcarbamoyl)oxy)but-2-enoate
2A

methyl (*Z*)-3-((dimethylcarbamoyl)oxy)but-2-enoate
2B



(*Z*)-4-oxopent-2-en-2-yl dimethylcarbamate
2C

benzyl (*Z*)-3-((dimethylcarbamoyl)oxy)but-2-enoate
2D

isopropyl (*Z*)-3-((dimethylcarbamoyl)oxy)but-2 enoate
2E

tert-butyl (*Z*)-3-((dimethylcarbamoyl)oxy)but-2-enoate
2F

SCHEME 6: **Synthesis of Enol Carbamate derivatives in the presence of a new Catalyst**

Conclusion

As an important result, the new nanomagnetic catalyst is much better than copper (II) acetate for use in our synthetic experiments. The amazing properties of Iron Oxide Nanoparticles (Fe_3O_4)-such as high surface area, magnetic properties, and low cost have led to widespread use in the synthesis of new catalysts. This magnetic nanocatalyst which we built, is harmless to the environment, and is easily separable from the products, and can take several reactions without losing its catalytic ability (recoverability). The synthesis of the new magnetic nanocatalyst has helped a lot to improve the conditions of reactions and has led to our products being synthesized with better efficiency. Besides, it saves time and thermal energy in various chemical reactions.

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