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Synthesis of Biaryl Compounds Using Copper Ferrite Nanoparticles

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Abstract

In the present work, the magnetic properties and catalytic properties of the $CuFe_2O_4$ nanoparticles have presented. The wet chemical synthesis technique was employed for the synthesis of $CuFe_2O_4$ catalyst. The crystallinity and phase purity of the $CuFe_2O_4$ nanoparticles were checked by the X-ray diffraction technique. The magnetic properties of the prepared copper ferrite catalyst were studied by pulse field hysteresis loop tracer technique at room temperature. The catalytic studies on the copper ferrite catalyst were carried for the preparation of biaryls of boronic acids using different solvents like methanol, THF, ethanol etc by a typical procedure. Copper ferrite was found to be a highly active catalyst for the Suzuki coupling reaction between arylboronic acids. The catalyst could be recovered easily by applying an external magnetic field.

Keyword: Copper ferrite; catalyst; biaryls; Suzuki reaction

INTRODUCTION:

Ferrites are the ferrimagnetic oxides which consists of the ferric oxide and metal oxide. Ferrites are of three types namely spinel ferrite, garnet and hexagonal ferrite [1-3]. Among the ferrites spinel ferrite are being interesting materials because of their numerous applications. The spinel ferrites can be employed in the fields of biomedical applications, gas sensors, targeted drug delivery, hyperthermia treatment and catalyst

[4-8]. Recently, the focus of the researchers is on the catalytic studies of the spinel ferrites [9]. The use of the spinel ferrites as a catalyst is advantageous because they are recyclable, reusable and cheaper. Recent reports reveal that magnetic nanoparticles are efficient catalysts and they can be easily separated from reaction mixture [10]. The high surface area to volume ratio of metal oxide nanoparticle is mainly responsible for their catalytic performance [11]. Copper ferrite nano material is one such reusable catalyst which shows profound catalytic activity in organic synthesis [12].
The aim of present work is to characterize the prepared copper ferrite nano particles for magnetic studies. Further, to investigate its catalytic performance in the synthesis of biaryl compounds of boronic acids.

Synthesis of the Copper ferrite catalyst
The nanoparticles of copper spinel ferrite were prepared by citric acid assisted sol-gel auto combustion method. The synthesis procedure adapted in the present work is discussed in detail in the earlier report [13].

Characterizations
The phase purity of the prepared copper ferrite nanoparticles was checked by the X-ray diffraction technique. Magnetic properties of the copper ferrite catalyst were systematically investigated by using pulse field hysteresis loop tracer technique at room temperature. Various parameters like saturation magnetization (Ms), coercivity (Hc), remanence magnetization (Mr), and remanence ratio (Mr/Ms) were calculated from M-H hysteresis plot.

RESULTS AND DISCUSSION

Magnetization
The various magnetic properties like saturation, magnetization, remanent magnetization and coercivity are estimated from the hysteresis curve. Figure 1 shows the hysteresis curve for $CuFe_2O_4$ nanoparticles measured at room temperature. The values of saturation magnetization, remanent magnetization and coercivity of the sol-gel synthesized copper ferrite particles are 24.47emu/gm, 19.47emu/gm and 1123.19 Oe respectively .These values of magnetic parameters are different compared to the bulk copper ferrite due to particle size effect.

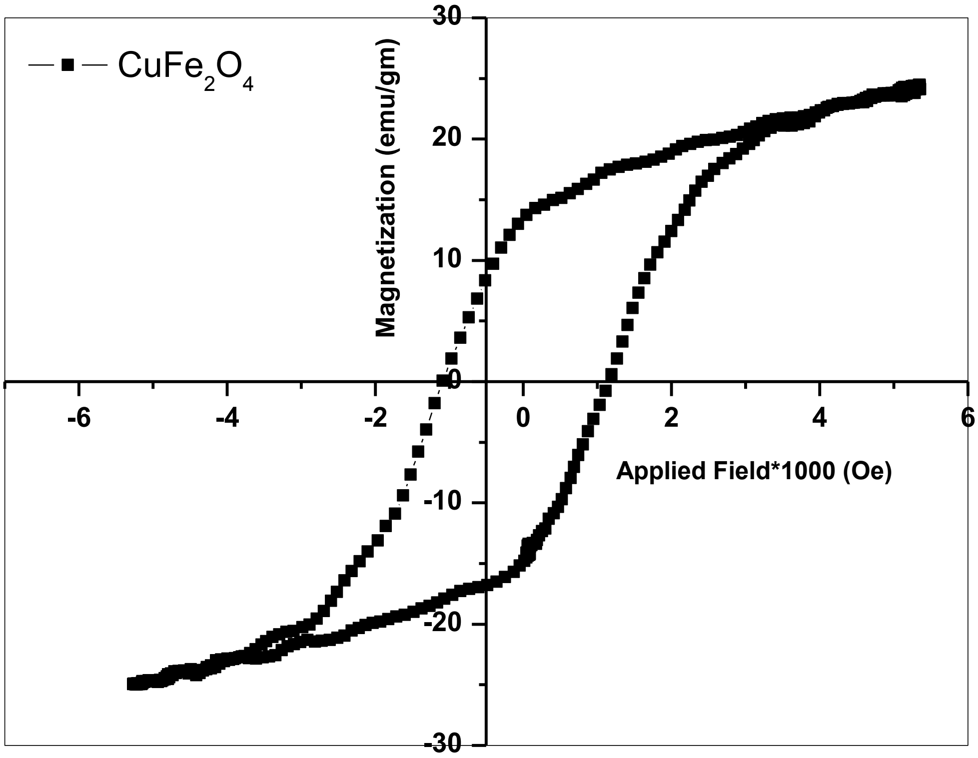

Figure 1: M-H plot of the copper ferrite catalyst

Catalytic performance of the copper ferrite

For catalytic applications of prepared copper ferrite, it has employed in the preparation of biaryl from boronic acids. Arylboronic acid (1 mmol) in a 5 mL methanol solvent was stirred at room temperature for different time periods ranging from 5-10h in the presence of 100 mg of Cu-ferrite catalyst. The reaction was monitored by TLC, after completion of reaction, the reaction mixture was diluted with 10 ml methanol and the catalyst was recovered by filtration. The obtained filtrate was concentrated, thereafter added 10 ml water and ethyl acetate to separate out the organic layer. The organic layer was dried over anhydrous sodium sulphate and concentrated to give the pure product. The reaction of biaryl formation is shown in figure 2.

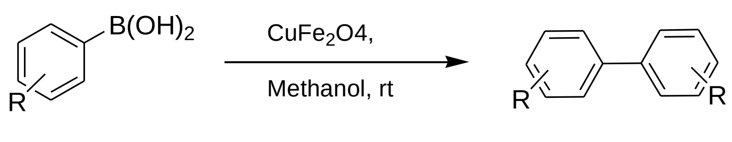

Figure 2: Reaction of biaryls formation

The reaction of aryl boronic acid is a coupling type of reaction and the reaction can be done under different solvents like methanol, ethanol, THF, Diethyl ether etc. The details about the biaryl formation using different solvents, with different time periods along with their yield are described in table 1.

Table 1: Solvent, biaryl product, time and yield

SR. No	Solvent	Biaryl product	Time (hr)	Yield
1	Methanol	Biaryl product	5	96
2	THF	Biaryl product	5	93
3	Ethanol	Biaryl product	7	91
4	Diethyl ether	Biaryl product	7	90

The data as given in table 1as recovery of product and reaction time suggest that the reaction carried out using methanol as solvent gives good result. The time required for the completion of the reaction is less as compared to that of using other solvents. It is observed that the yield produced is maximum when the methanol was used as a solvent. The reusability of the catalyst was also studied for coupling reaction tested. The percentage of the recovery of catalyst after reaction completion, the yield of the product and the temperature used for the reaction were tabulated in the table 2. One can observe from table 2 that the recovery of the catalyst is in the range of 82-96% which is comparatively high. Also the yield ranges from 88-94% at room temperature.

Table 2: Catalyst recovery, yield and temperature

Sr. No	Catalyst Recovery	Yield	Temp
1	-	94	RT
2	96	92	RT
3	85	90	RT
4	82	88	RT

CONCLUSION

The copper ferrite catalyst was successfully prepared by sol-gel auto-combustion method. The ferromagnetic nature of the copper ferrite nanoparticles was revealed by the pulse field hysteresis loop tracer technique. The magnetic parameters obtained from the M-H plot are in reported range. The catalytic properties of the copper ferrite nanoparticles were studied by synthesizing biaryls. The recovery of catalyst nanoparticles after completion of reaction is maximum. The catalyst recovered by filtration and washed with distilled water is almost 82-96 %. The reusability of catalyst is tested 3-4 times for the same reaction and it is found that copper ferrite is reusable up to 90%.

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