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Synthesis of metal spinel type of ferrite and used as a catalysts in organic reactions

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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.

Keywords: ferrite, catalyst; biaryl

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].

Ferrites have been studied extensively due to their low prices, easy to fabricate and abundant uses in technological and industrial applications^[13-15].

The useful properties of the spinel ferrites mostly depend upon the chemical composition, preparation methods sintering temperature, nature of the additives their distribution i.e tendency to occupy tetrahedral (A) or octahedral (B) sites^[16]. In many commercial applications, like transformer cores, chokes, high density recording, microwave devices etc.

The copper catalyst used for the strategy of the synthesis of rare nitrogen-linked seven-, eight- and nine membered biaryl ring systems of previous data. It is proposed that the reaction proceeds through a highly activated intramolecularly co-ordinated copper catalyst.^[17]

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.

Ferrites are chemical compounds which are composed ceramic material and iron oxide as their main component. ferromagnetic ceramic compound, ferrites has a spinel type structure. the magnetic properties of ferrite is due to structure and the distribution arrangement of the ions sub lattice. most of the ferrite has a spinel structure with formulae AB_2O_4 , where "A" Divalent ions such as Mg^{2+} , CO^{2+} , Ni^{2+} , Mn^{2+} and "B" are the trivalent ions Fe^{3+} and Al^{3+} . spinels structure have and oxygen ion sub lattice, cubic closed packed arrangement with cation occupying various combinations of the octahedral and tetrahedral sides the cubic unit cell contain 8 formula unit and containing 32 octahedral and 64 tetrahedral sites. spinel are basically categorized in to a normal and inverse spinel. in normal spinel, the divalent cation "A" are position are tetrahedral site and the trivalent cation B on octahedral site NiFe_2O_4 or CoFe_2O_4 has An inverse spinel crystal structure. inverse spinel A cation occupies one half

the octahedral coordination site and half of the B cation occupy the other half octahedral sites as well as all tetrahedral site [18-20].

Synthesis of the Copper ferrite catalyst

The nanoparticles of copper spinel ferrite were prepared by citric acid assisted sol-gel auto combustion method.

Synthesis of Copper ferrite catalyst

The wet chemical route of the synthesis was employed for the preparation of the copper ferrite nanoparticles. The nanocrystalline sample of copper ferrite (CuFe_2O_4) is prepared by using the sol-gel auto-combustion method. The analytical grade nitrates of copper, ferric and citric acid as a fuel were mixed as per stoichiometric proportions. The stoichiometric proportions of metal nitrates to fuel (citric acid) ratio as 1:3 were taken into separate glass beakers. These were stirred for 15-20 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 80 – 90 °C for 6 h on a hot plate. On the formation of sol, gel, very viscous gel the temperature was further raised up to 120 °C so that the auto combustion started and finally fine powder was obtained. The as prepared powder was ground and sintered at temperature 7000C for 6h. The sintered nanoparticles of the copper were used for further characterization and catalytic studies.

Characterization of copper ferrite catalyst

The structural characterizations of the prepared copper ferrite were done by using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The morphological studies were carried out using scanning electron microscopy technique. The magnetic properties of the prepared ferrite catalyst were studied by using the pulse field hysteresis loop tracer technique at room temperature. Further, the recovery of catalyst is checked after filtration of the catalyst [21-22].

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 (M_s), coercivity (H_c), remanence magnetization (M_r), and remanence ratio (M_r/M_s) 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.

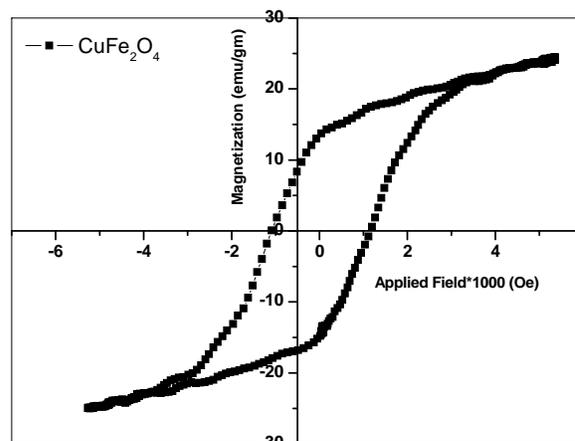


Fig 1: M-H plot of the copper ferrite catalyst

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.

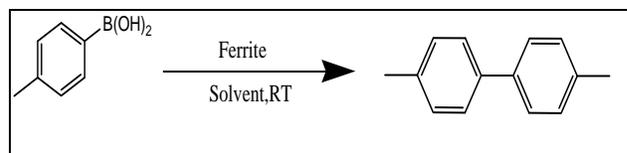


Fig 2: Reaction of biaryls formation

The reaction of Substituted aryl boronic acid is a coupling type of reaction and the reaction can be done under different solvents like THF, ethanol, DCM, methanol etc. we have checked the recovery of product and reaction time suggests that the reaction carrying out by using methanol as solvent gives excellent results. 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 checked by these types of reactions for several times and it gives good recovery for 3-4 cycles and excellent results for these coupling products. The percentage of the recovery of catalyst after reaction completion, the yield of the product and we have observe that the recovery of the catalyst is in the range of 83-96% which is comparatively high. Also the yield ranges from 88-94% at room temperature for the coupling reaction for the same catalyst of ferrites. We have checked this coupling reaction for different temperature and carried out same reaction, but got the good result at room temperature. So this reaction don't need heating, so need to apply for heating or energy source so this reaction is happens at stirring.

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 and nickel ferrites are reusable up 90-92 Percentages, and specifically the nickel ferrites gives good results with same reaction, so further procedure of product in process. So our copper ferrites catalyst gives the excellent yield, good purity with excellent recovery of catalyst. We will be using coupling products for the bioactivity for different microorganism and cells. The reaction time required for this coupling type of reaction is 5 hour for stirring and up to 7 hours maximum for completion of this Suzuki type of coupling reactions. The Suzuki coupling reaction is done by using nanoparticles of copper, it will be used for the biological activities and we get some antioxidant activities of catalyst and now we will have some in processes of bioactivity of catalyst for antifungal, antimalarial, anticancer, antiviral and etc.

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