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ARTICLE

Use of Some Metal Ferrites as Catalyst in Aldol Condensation Reaction

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ABSTRACT

Two moles of benzaldehyde and one mole of acetone were condensed to afford dibenzalacetone in presence of sodium hydroxide. This aldol condensation was carried out in presence of magnetic copper ferrite, CuFe_2O_4 , which was synthesized by hydrothermal method. Other magnetic ferrites (where $M = \text{Ni, Co, Zn}$ and Mg) were also prepared. As-prepared metal ferrites were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The copper ferrite was observed to be square shaped and particle size was 29.71 nm. The yield of product (dibenzalacetone) in presence of copper ferrite was found to be highest (90.6%). A comparative study was made with different metal ferrites as catalyst and found that the activity of metal ferrites followed the order:



KEYWORDS

Aldol condensation, Copper ferrite, Catalyst, Synthesis, Hydrothermal method.

INTRODUCTION

The aldol reaction is one of the most powerful tools in organic synthesis for the formation of carbon-carbon bonds. Not only this, it allowed generation of many stereo-centers in the product and therefore, it is interesting from the synthetic point of view for most of the organic chemists. Tang *et al.* [1] synthesized and used L-proline amides (organocatalyst) for catalyzing the direct aldol reaction of acetone with 4-nitrobenzaldehyde. It was observed that catalysts with strong electron withdrawing groups exhibited higher catalytic activity and enantioselectivity as compared to analogues with electron-donating groups. Watanabe & Seto [2] investigated the catalytic effect of barium ferrite (magnetic particles) on aldol condensation. They also examined the poisoning effect of different oxoacid ions. The tungstate and molybdate ions were found to exhibit more deactivation of this catalysis.

An efficient and reusable nanocatalyst Fe_3O_4 , *p*-amino-benzoic acid Cu(II) magnetic nanoparticle were also reported and found that as-prepared superparamagnetic nanoparticles were in the range of 10–20 nm [3]. Their catalytic activity and performance for the synthesis of 5-arylidene-2-imidazolidine-2, 4-dione and 5-arylidenthiazolidine derivatives *via* aldol cond-

ensation reactions was observed. Pazoki *et al.* [4] synthesized BiPO₄ decorated with Ni–Fe layered double hydroxide (BiPO₄@Ni–Fe LDH), which was then used as a catalyst for aldol condensation of aldehydes and carbonyl compounds with good yields using glycerine as a green solvent.

Fattahi *et al.* [5] prepared tetramethylguanidine supported onto magnetic Fe₃O₄ nanoparticles (MNPs-TMG) and used as-synthesized catalyst for the aldol reaction between various aldehydes and acetone to afford β-hydroxy carbonyl compounds with high yields. The α-alkylation of various nitriles with carbonyl compounds was successfully carried out by Motokura *et al.* [6] using a multifunctional catalyst, where palladium nanoparticles were supported on hydrotalcite. The alkylated nitriles were formed through aldol reaction at basic sites available on the hydrotalcite surface and followed by hydrogenation on the palladium nanoparticles.

Senapati & Phukan [7] synthesized spinel cobalt ferrite magnetic nanoparticles and found that their average particle size was in the range of 40-50 nm, when a combination of coprecipitation and sonochemical technique was applied without using any surfactant or organic capping agent. The uncapped nanoparticles were used directly for aldol reaction in ethanol. Wu *et al.* [8] prepared magnetic solid acid catalysts SO₄²⁻/Zr(OH)-Fe₃O₄ nanoparticles. It was observed that aqueous asymmetric aldol reaction of different benzaldehydes with strong electron withdrawing groups in presence of as-prepared catalyst such as CN and NO₂ exhibited good to excellent catalytic performance. Alminshid *et al.* [9] used MgO as catalyst for the activation of aldol condensation reaction of acetone to form diacetone alcohol. It was revealed that the OH group played a role of suppression agent on MgO surface so that further dehydration of diacetone alcohol to mesityl oxide is controlled. Saiyed & Bedekar [10] synthesized a series of chiral amino oxazolines as organocatalysts and used for aldol reactions (asymmetric intermolecular) between aromatic aldehydes and acetone. It was observed that this reaction can be carried out with a wide range of aromatic aldehydes with good to high selectivity.

EXPERIMENTAL

Synthesis of copper ferrite nanoparticles: Hydrothermal method was used to prepare copper ferrite following a similar method as reported by Naidu & Madhuri [11]. Copper nitrate [Cu(NO₃)₂] and ferric nitrate [Fe(NO₃)₃·9H₂O] were used as precursor of copper and iron, respectively. A Teflon coated autoclave was used for this purpose. Copper and iron nitrates were dissolved in distilled water keeping the ratio of nitrates and water as 1:3. The resultant solution was stirred and NaOH was added dropwise into the solution in 1:4 ratio till the pH was maintained at 11. The mixture was vigorously stirred for 2 h and transferred into Teflon coated stainless steel autoclave and sealed. Then autoclave was heated at 150 °C for around 48 h. After heating, the autoclave was allowed to cool at room temperature. The product in the autoclave was filtered and washed several times from water and then acetone, till its pH reaches 7.

Aldol reaction catalyzed by copper ferrite: A mixture of benzaldehyde (2.5 mL) and acetone (0.9 mL) in molar ratio of 1:2 and copper ferrite (nanocatalyst) (0.05 g) was stirred at

40-60 °C. The NaOH pellets (2.5 g) dissolved in 25 mL water and then 20 mL of ethanol was added into the flask. Then, it was added drop by drop into the mixture of benzaldehyde and acetone and stirred continuously for 25-30 min. After 30 min, a yellow precipitate was observed. The solution was filtered with suction and washed thoroughly with water to remove excess of alkali. The crude product was added to 50-100 mL ethyl acetate. Thereafter, magnesium sulphate was added and filtered. The solvent was removed with rotatory evaporator. The product was recrystallized with minimum amount (< 5 mL) of warm ethyl acetate. The product was filtered under suction affording yellow crystals (**Scheme-I**).

RESULTS AND DISCUSSION

FESEM studies: The as-prepared copper ferrite particles were characterized by scanning electron microscope (SEM) on JSM-6100 (JEOL) with a digital image processor. According to the SEM image (Fig. 1), the morphology of copper ferrite was found to be square shaped.

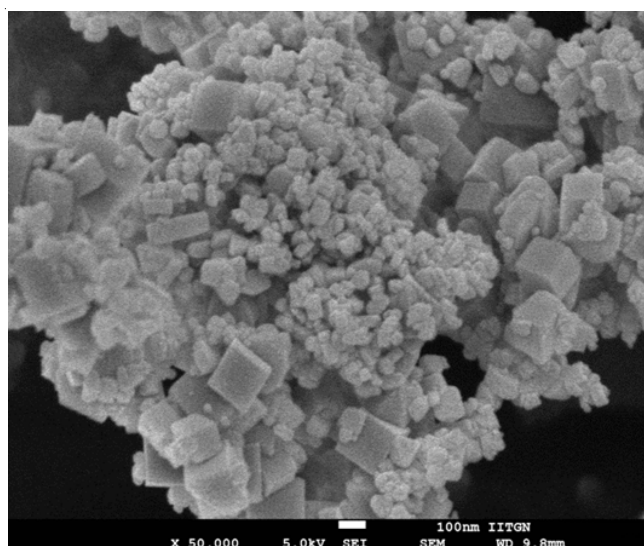


Fig. 1. FESEM image of copper ferrite

XRD studies: The XRD spectrum of the copper ferrite crystal was acquired by employing a X' Pert Pro XRD equipped with X' Celerator solid state detector. The crystalline nature of the synthesized copper ferrite sample was observed by X-ray diffraction pattern (Fig. 2). The average particle size of the particles was calculated by Debye-Scherrer's equation and found to be in the nano-range (29.71 nm).

XPS studies: X-Ray photoelectron spectral analysis was also carried out using a Thermo Kα + X-ray spectrometer. The contact angle measurement was carried out using a KRUSS drop shape analyzer, which gives Cu, Fe and O in 2p³, 2p and 1s states, respectively (Fig. 3).

EDX studies: Energy-dispersive X-ray spectroscopy with JSM 7600 F (Jeol) showed the peaks for Fe, Cu and O, only which indicates that copper ferrite is in pure state and it does not contain any impurity (Fig. 4).

FTIR studies: FTIR spectrometer RX-I was used to record IR spectrum of the synthesized organic product. A band is observed in the region 3010-3000 cm⁻¹ for aromatic C-H

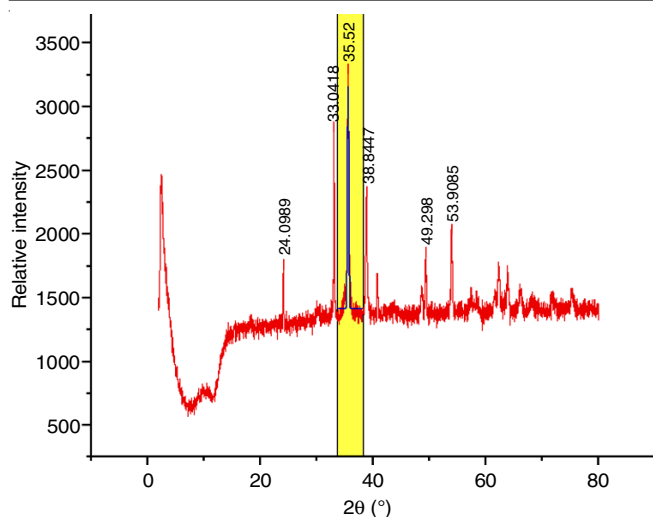


Fig. 2. Powder XRD pattern of copper ferrite

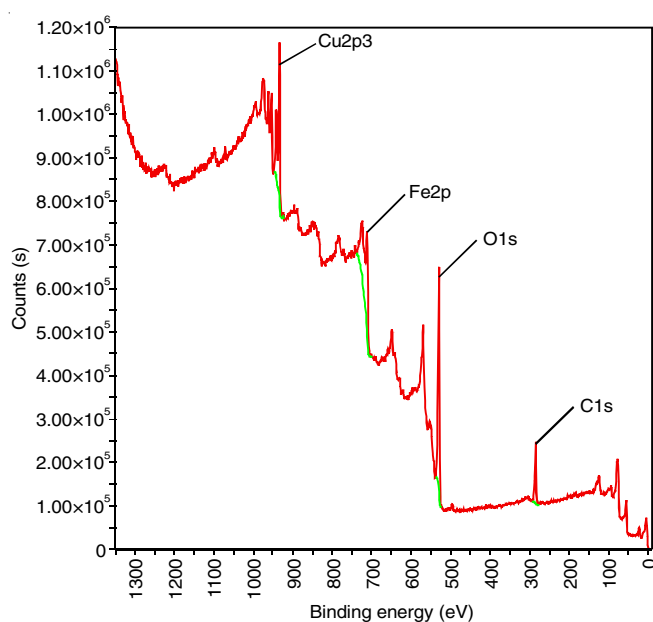


Fig. 3. XPS analysis of copper ferrite

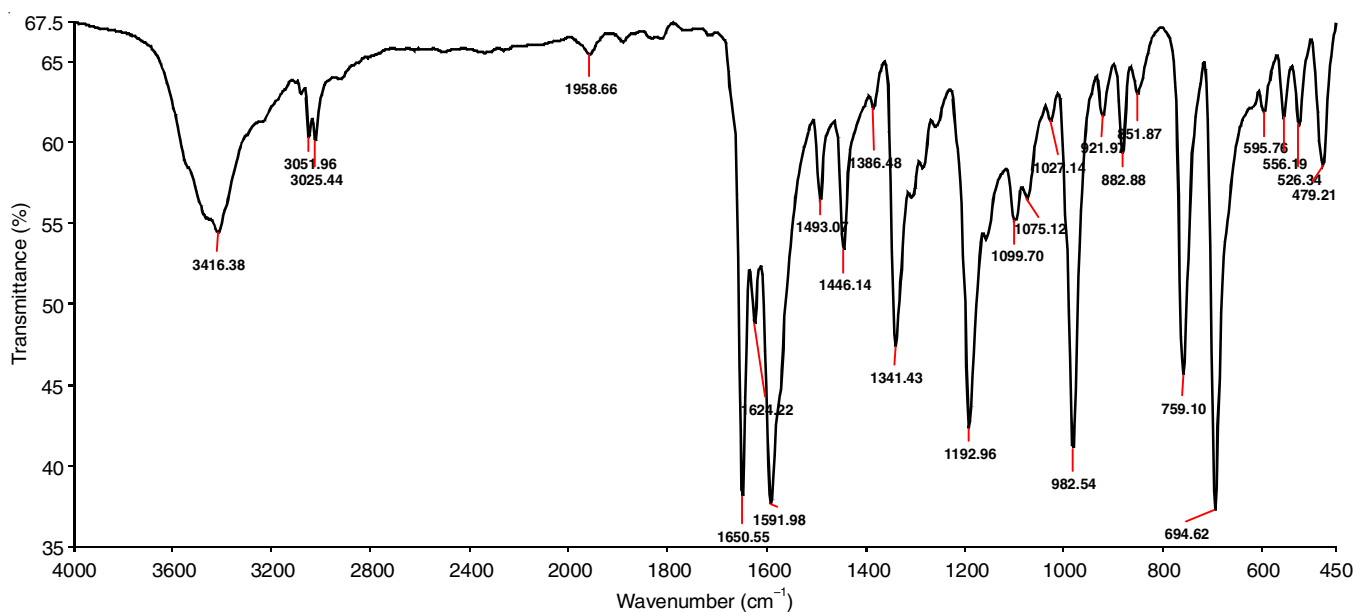


Fig. 5. FTIR spectrum of product

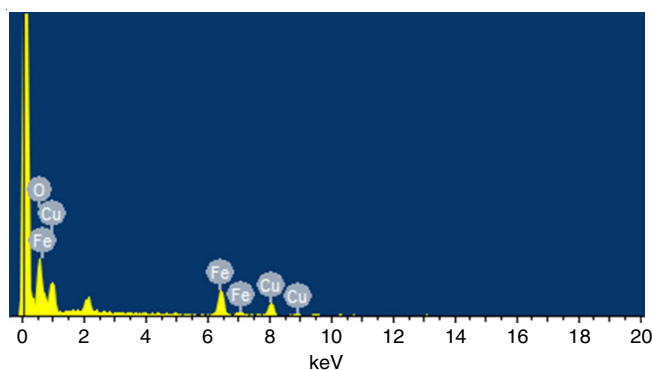


Fig. 4. EDS analysis of copper ferrite

stretching vibration. Moreover, bands appearing at 3052-3025 cm^{-1} may be assigned to C-H vibration in aromatic system; bands at 1193, 1100 and 1075 cm^{-1} may be attributed to CH in-plane bending vibration while bands at 922, 851, 759 and 659 cm^{-1} due to C-H out of plane bending vibrations. Presence of a strong band at 1650 cm^{-1} is due to C=O vibrations. There are some additional bands for C=C stretching vibrations at 1650 and 1625 cm^{-1} (also due to C=O vibrations) whereas C-C stretching vibrations were observed at 1592, 1493 and 1446 cm^{-1} (Fig. 5). All these bands supported that the product is dibenzalacetone and these results are in conformity with the results reported earlier [12].

NMR studies: FT-NMR spectrometer model Advance-II (Bruker) (400 MHz) was used to record NMR spectrum of the product. The NMR spectrum of the synthesized organic product indicated signals (doublets) in the range of δ 7.76-7.73 and 7.11-7.08 ppm. These two doublets were due to the presence of olefinic protons. Signals were in the form of doublet because one olefinic C-H is attached to C=O group while other CH groups is attached to phenyl group. The doublet at δ 7.08-7.01 ppm may be assigned to the olefinic proton attached to carbonyl group while signal at δ 7.76-7.73 ppm are due to C-H attached to the phenyl group. There are two more signals in the ratio of δ 2:3 at 7.63 and 7.44 ppm and these are due to

aromatic protons at *o*- and (*m*- & *p*-) positions (Fig. 6). These NMR data are also in the accordance of dibenzalacetone as product. The results are similar to as-obtained by Sudha *et al.* [12].

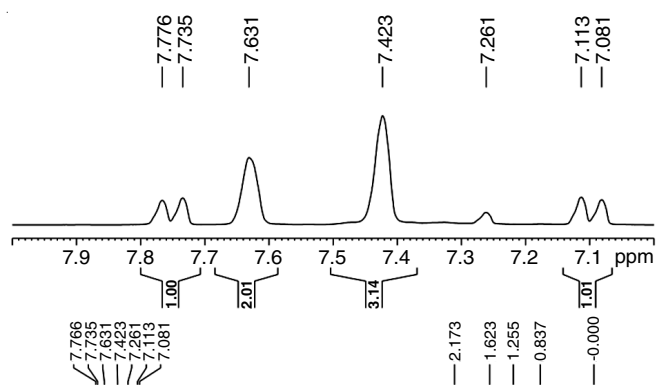


Fig. 6. NMR spectrum of product

Comparitive study of Aldol reaction: Different parameters were varied such as pH, amount of solvent, amount of catalyst, *etc.* to achieve the optional conditions. The effect of benzaldehyde was observed in the range of 1.5-3.5 mL and results are reported in Table-1. It was observed that as the amount of benzaldehyde was increased while keeping other parameters constant, then the yield increases up to 2.5 mL of benzaldehyde and showed a declining behaviour above 2.5 mL. It may due to the fact that 2.5 mL is the required amount of benzaldehyde, above which it remain unreacted.

TABLE-1
EFFECT OF BENZALDEHYDE

Benzaldehyde (mL)	Acetone (mL)	NaOH (g)	Copper ferrite (g)	Yield (%)
1.5	0.9	2.5	0.08	5.6
2.0	0.9	2.5	0.08	16.2
2.5	0.9	2.5	0.08	90.6
3.0	0.9	2.5	0.08	55.8
3.5	0.9	2.5	0.08	61.0

Effect of amount of acetone was observed by varying the amount from 0.3 to 0.15 mL and results are shown in Table-2. It was observed that as the amount of acetone was increased, the yield increases up to 0.9 mL of acetone. It may be due to the fact that 0.9 mL is the requisite amount of acetone, which favoured the direct formation of the conjugated enone group. Similar factor has be observed in case of NaOH also and the result are shown in Table-3. It was observed that as the amount of NaOH was increased keeping other parameter constant, then the yield increases up to 2.5 g of NaOH.

TABLE-2
EFFECT OF ACETONE

Acetone (mL)	Benzaldehyde (mL)	NaOH (g)	Copper ferrite (g)	Yield (%)
0.3	2.5	2.5	0.08	8.2
0.5	2.5	2.5	0.08	27.5
0.9	2.5	2.5	0.08	90.6
1.2	2.5	2.5	0.08	72.3
1.5	2.5	2.5	0.08	30.4

TABLE-3
EFFECT OF NaOH

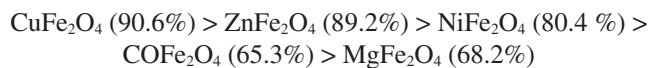
Acetone (mL)	Benzaldehyde (mL)	NaOH (g)	Copper ferrite (g)	Yield (%)
0.9	2.5	0.475	0.08	17.5
0.9	2.5	1.270	0.08	20.1
0.9	2.5	1.570	0.08	64.8
0.9	2.5	2.000	0.08	29.6
0.9	2.5	2.500	0.08	90.6
0.9	2.5	3.000	0.08	35.1

The effect of copper ferrite (catalyst) was observed in the range of 0.05-0.015 g and the results are given in Table-4. It was found that the formation of organic product dibenzalacetone increases on increasing amount of copper ferrite up to 0.08 g because more active sites are available, but yield of the product started decreasing above 0.08 g. It may be attributed to the fact that all active sites are occupied and as a result, yield decreases.

TABLE-4
EFFECT OF COPPER FERRITE

Acetone (mL)	Benzaldehyde (mL)	NaOH (g)	Copper ferrite (g)	Yield (%)
0.9	2.5	2.5	0.050	44.8
0.9	2.5	2.5	0.080	90.6
0.9	2.5	2.5	0.010	69.4
0.9	2.5	2.5	0.015	41.9

A comparative study was also carried out to compare the efficacy of different metal ferrites for aldol condensation, which followed the order:



Conclusion

The CuFe_2O_4 nanoparticles were prepared with an average size of 29.71 nm *via* hydrothermal process in a Teflon coated autoclave. These nanoparticles were used as catalyst in presence of NaOH for aldol condensation of benzaldehyde and acetone under mild conditions. Some of the important advantages of this method are high yield, less time and mild reaction conditions. Using copper ferrite as environment friendly catalyst, the process is easy and can be reused 5-6 times without any significant loss of catalytic activity.

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