__Original Research Article__

USE OF SOME METALFERRITES AS CATALYST IN BENZIL-BENZILICACID REARRANGEMENT REACTION

ABSTRACT

Magnesium ferrite was used to catalyse the Benzil-Benzilic acid rearrangement reaction of 1,2-rearrangement of 1,2-diketones to α-hydroxy carboxylic acids in presence of a base. Magnesium ferrite was prepared by hydrothermal process. It was characterized by Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction Spectroscopy (XRD), and Energy Dispersive X-Ray Spectroscopy (EDX). The crystalline size of magnesium ferrite was found to have 82.47nm and these are irregular in shape. It was found that the yield of the product (benzilic acid) in the presence of Mg ferrite was 81.6%, which is almost 2.3 times the yield obtained in the absence of catalyst. A comparative study was made with different metal ferrites as catalyst and it was found that the activity of metal ferrites followed the order:

$$MgFe_2O_4 > Cu\ Fe_2O_4 > Ni\ Fe_2O_4 > Co\ Fe_2O_4 > Zn\ Fe_2O_4$$

Keywords: Benzil-Benzilic acid rearrangement reaction, Magnesium ferrite, Catalyst, Synthesis, Hydrothermal method

INTRODUCTION

Odagi et al.[1] reported an enantioselective synthesies of the norhasubanan alkaloid (+)-stephadiamine and hasubanan alkaloid (−)-metaphanine. It involves diastereoselective oxidative phenolic coupling reaction, which was followed by regioselective intramolecular aza-Michael reaction, affording hasubanan skeleton. It was observed that (-)-metaphanine is easily converted to (+)-stephadiamine through aza-benzilic acid type rearrangement.

Wu et al.[2] reported catalytic enantioselective benzilic ester rearrangement. Reaction of 2,3-diketoesters with alcohols afforded structurally diverse α- aryl(alkyl) substituted-α-hydroxymalonates. It was observed that in presence of a catalytic amount of Cu (OTf)$_2$ and a chiral box ligand, this reaction proceeds under mild conditions and afforded good to excellent yields with high enantioselectivites.

Xiao et al.[3] carried out synthesis of anti-HIV (-)-isatisine A in eight steps from indole and 4,6-*O*-isopropylidene-protected glucal. Indole *C*-furanoside was derived from indole *C*-glucoside via a ring contractive benzilic acid rearrangement. The biogenetic hypothesis was supported by model studies that the *O*-glucoside was converted to *O*-furanoside through benzilic acid rearrangement.

Schwiderski and Kruse[4] investigated catalytic effect of the Brønsted acid, Brønsted base and the Lewis acid on the conversion of biomass derived carbohydrates. One of the example is of the glycolaldehyde conversion. It was reported that the Lewis acid catalyzes the dehydration, ketol-endiol-tautomerism, retro-aldol-reaction and also benzilicacid rearrangement. The main products obtained were C_4- and C_6-carbohydrates along with some secondary products 2-hydroxybut-3-enoic acid and furans.

MATERIALS AND METHODS

Materials:

Magnesium nitrate hexa hydrates (SRL) was utilized with a purity of 99% and NaOH (98%) for the production of nanoparticles. Benzaldehyde, malonic acid and liquid ammonia were procured from Rankem, and Fischer scientific respectively.

Synthesis of Magnesium ferrite nanoparticles:

A hydrothermal approach similar to that employed by Naidu and Madhuri **[5]** was utilized to synthesize magnesium ferrite using a Teflon-coated autoclave. Magnesium nitrate hexahydrate and ferric nitrate nanohydrate were utilized as magnesium and iron precursors, respectively. Magnesium and iron nitrates were dissolved in distilled water in a nitrate: water ratio 1:3. The resulting solution was stirred, and then NaOH was added drop by drop in 1:4 ratios until the pH reached 11. After rapid stirring for 2 h, the liquid was moved to a Teflon-coated stainless steel autoclave and sealed. The autoclave was then heated to 150°C for about 48 h. The autoclave was allowed to cool at ambient temperature after heating is over.

RESULTS AND DISCUSSION

Field Emission Scanning Electron Microscopy (FESEM):

The JSM-6100 (JEOL) with a digital image processor was used to record FESEM to know the morphology of as-prepared magnesium ferrite particles. The FESEM images are shown in figure 1.

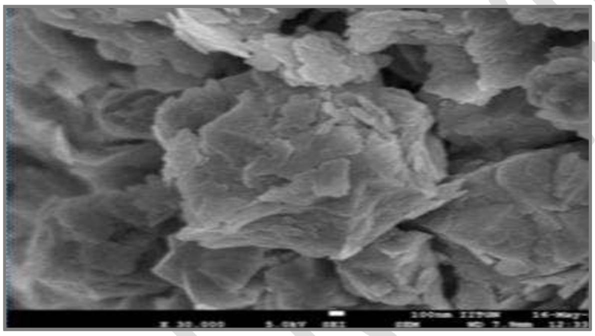


Figure1. FESEM Image of magnesium ferrite.

It was observed that these magnesium ferrite particles are having a nanoflower like structure.

X-Ray Diffraction (XRD):

A x· Pert Pro XRD equipped with an X' Celebrator solid state detector was used to record X-ray diffraction pattern. The XRD of magnesium ferrite revealed the crystalline character of this sample. The result tare reported in figure 2.

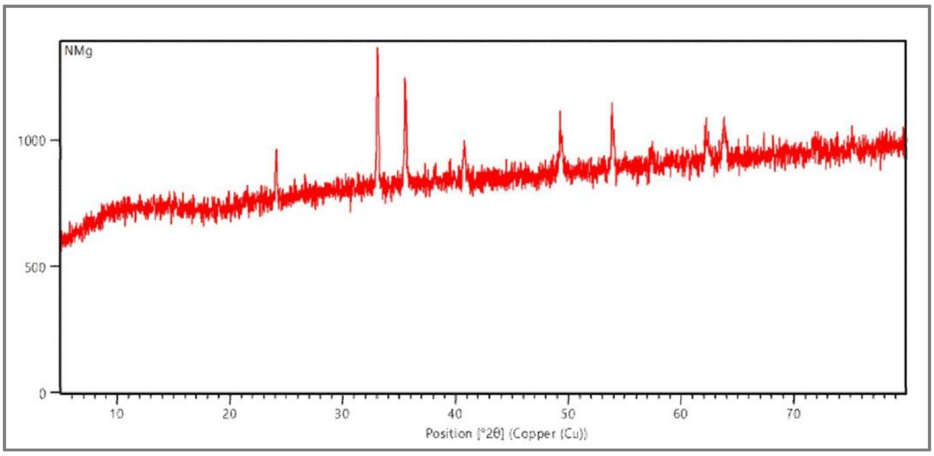


Figure 2. XRD pattern of magnesium ferrite.

The Debye-Scherrer equation was used to compute the average particle size of particles, which was found to be in the nano-range (82.47 nm).

X-Ray Photoelectron Spectroscopy (XPS):

A Thermo K-alpha+X-ray spectrometer was used for X- ray photoelectron spectral analysis. A KRUSS drop shape analyzer was used to measure the contact angle. XPS of magnesium ferrite indicated that Mg, Fe, and O are present in Is, 2p, and ls states, respectively in this sample.

Energy-Dispersive X-Ray Spectroscopy (EDX):

Energy-dispersive X-ray spectrum was recorded with JSM 7600 F (Jeol). The results are reported in figure 3.

The EDX of magnesium ferrite revealed peaks for Mg, Fe and O only, which indicated that the sample of magnesium ferrite is pure and free of any impurity.

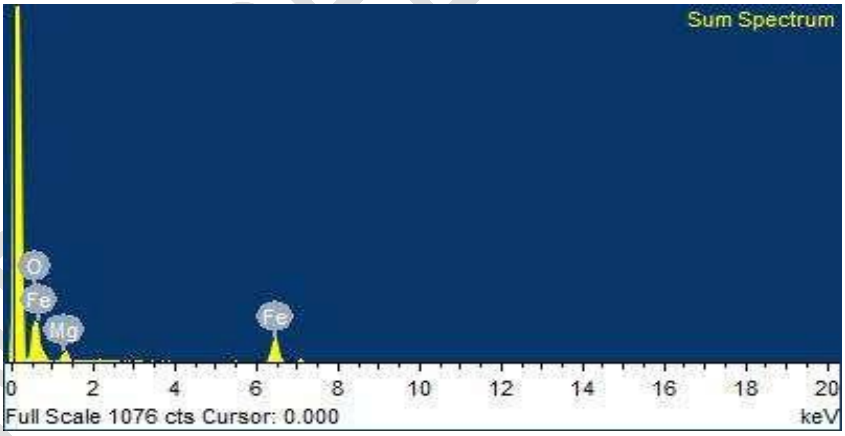
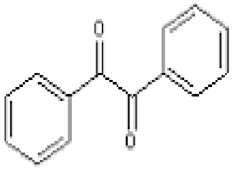
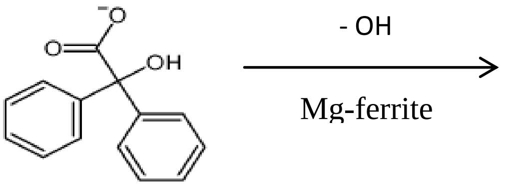


Figure.3. EDX spectrum of magnesium ferrite.

Benzil- Benzilic acid rearrangement catalyzed by magnesium ferrite-





Yield (40.37%)

The potassium hydroxide pellets (5 g) was dissolved in 10 mL of water and 15 mL of ethyl alcohol and magnesium ferrites (0.10 g) were added to this solution under stirring. Then 5 g of pure benzyl was added and it was boiled for 10 to 15 minutes. The content of the flask was transferred into a small beaker or a procelain dish. It was allowed to settle for many hours until all of the potassium benzilate was crystallised. Conc. HCl (8 mL) was added to dissolve potassium benzilate in 50 mL of water. It was filtered with ice-cold ethanol. The obtained product was washed with water, air dried and then recrystallized.

Fourier transform infrared (FTIR) spectrum:

The FTIR Spectrometer RX-I was used to recored IR spectrum of the product. The spectrum is given in Figure-4

Figure-4: FT-IR Spectrum of product

A band at 3398 cm^{-1} indicated the presence of -OH stretching vibration while another band at 3063 cm^{-1} is due to -CH stretching vibration in aromatic system. A band at 1761 cm^{-1} may be due to C=O in carboxylic group. Bands at 1172 cm^{-1} may be attributed at -CH in-plane bending vibration while bands at 929, 874, and 770 cm^{-1} are due to -CH out-of-plane benzene vibration. The presence of bands at 1667 and, 1695 cm^{-1} may be due to C=C and C=O vibrations.

- **Fourier transform nuclear magnetic resonance spectrum**

FT-NMR spectrometer model Advance-II (Bruker) (400 MHz) was used to record NMR spectrum of the product.

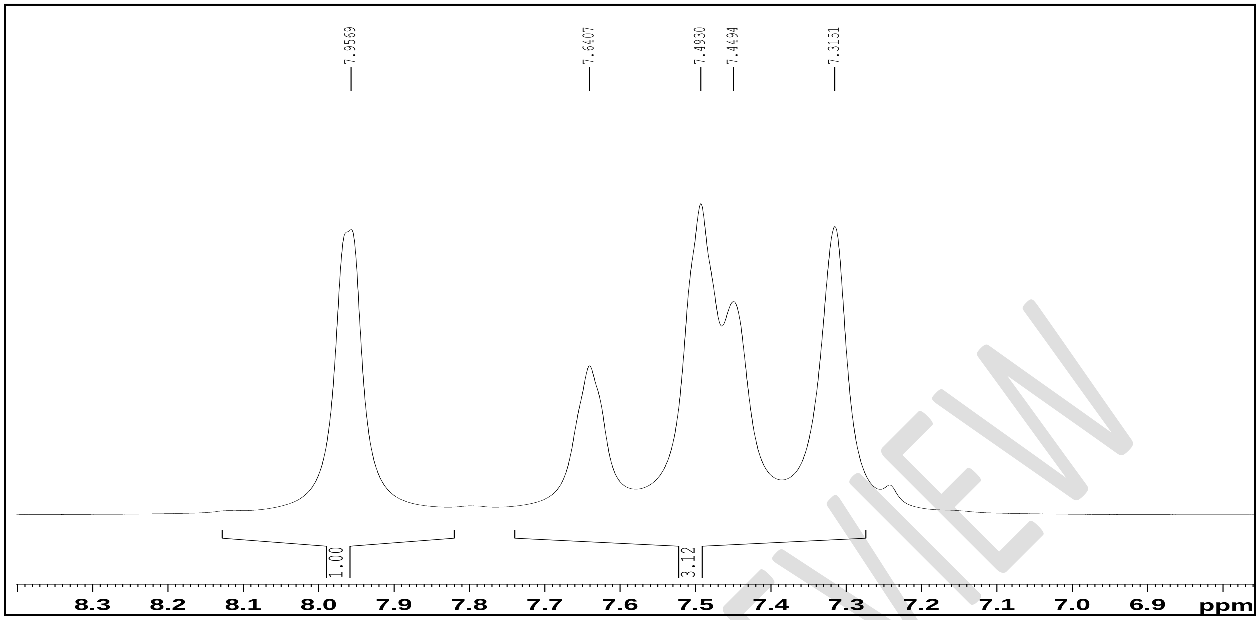


Figure-5: FT-NMR Spectrum of product

NMR spectrum of the product indicated signals in the range 7.31 δ (doublet) at 7.44- 7.49 δ. Two more signals at 7.64-7.95 δ may be due to different aromatic protons.

The product was confirmed as potassium benzilate on the basis of FT-IR and FT-NMR data. It was also confirmed by m.p. and m.m.p.

Effect of Different Parameters

Different factors were varied to achieve optimal conditions such as amount of benzil, ethyl alcohol, potassium hydroxide, catalyst, etc. The effect of benzil was observed in the range of 3.0-8.0 g. The results are shown in Table .1.

Table .1: Effect of benzil

Benzil (g)	**Potassium hydroxide (g)**	**Ethyl alcohol (mL)**	**Magnesium ferrite (g)**	**Yield (%)**
3.0	5.0	15.0	0.10	30.1

4.0	5.0	15.0	0.10	54.2
5.0	5.0	15.0	0.10	81.6
6.0	5.0	15.0	0.10	64.8
7.0	5.0	15.0	0.10	50.2
8.0	5.0	15.0	0.10	31.7

It was observed that when the amount of benzil was increased keeping other parameters constant, then the yield increases up to 5.0 g of benzil and then showed a declining behavior above 5.0 g. It may due to the fact that the 5.0 g is the required amount of benzil, above which it remains unreacted.

The effect of potassium hydroxide was observed in the range of 2.5-7.0 g. The results are shown in Table -2

Table -2: Effect of potassium hydroxide

Benzil (g)	**Potassium hydroxide (g)**	**Ethyl alcohol (mL)**	**Magnesium ferrite (g)**	**Yield (%)**
5.0	2.5	15.0	0.10	33.4
5.0	3.0	15.0	0.10	48.3
5.0	4.0	15.0	0.10	61.2
5.0	5.0	15.0	0.10	81.6
5.0	6.0	15.0	0.10	64.2
5.0	7.0	15.0	0.10	42.3

It was observed that when the amount of potassium hydroxide was increased keeping other parameters constant, then the yield increases up to 5.0 g of potassium hydroxide and then showed a declining behavior above 5.0 g. It may be due to the fact that 5.0 g is the required amount of potassium hydroxide for maintaining desired pH.

The effect of ethyl alcohol was observed in the range of 10.0-25.5 mL. The results are shown in Table -3.

Table-3: Effect of ethyl alcohol

Benzil (g)	**Potassium hydroxide (g)**	**Ethyl alcohol (mL)**	**Magnesium ferrite (g)**	**Yield (%)**
5.0	5.0	10.0	0.10	47.8
5.0	5.0	12.5	0.10	65.3
5.0	5.0	15.0	0.10	81.6
5.0	5.0	17.5	0.10	62.7
5.0	5.0	20.0	0.10	51.0
5.0	5.0	25.5	0.10	38.2

It was observed that when the amount of ethylalcohol was increased keeping other parameters constant, then the yield increases up to 15.0 mL of ethylalcohol and then showed a declining behavior above 15.0 mL. It may due to the fact that the 15.0 mL is the required amount of ethylalcohol, above which it remains unreacted.

The effect of magnesium-ferrite was observed in the range of 0.05- 0.15 g. The results are shown in Table -4.

Table -4: Effect of magnesium ferrite

Benzyil (g)	Potassium hydroxide (g)	Ethyl alcohol (mL)	Magnesium ferrite (g)	Yield (%)
5.0	5.0	15.0	0.05	38.3
5.0	5.0	15.0	0.08	60.0
5.0	5.0	15.0	0.10	81.6
5.0	5.0	15.0	0.11	67.2
5.0	5.0	15.0	0.13	50.4
5.0	5.0	15.0	0.15	40.4

It was observed that when the amount of magnesium ferrite was increased keeping other parameters constant, then the yield increases up to 0.10 g of magnesium ferrite and then showed a declining behavior above 0.10 g.

It may be attributed to the fact that all active sites are occupied (saturated state) and as a result, yield decreases.

The highest yield of benzilie acid could be obtained under the following optimum conditions:

Benzil = 5.0 g, Ethyl alcohol = 15.0 mL, KOH = 5.0 g, Mg- ferrite = 0.10 g

A comparative study was also carried out to compare the efficacy of different metal ferrites for benzilic acid rearrangement reaction, which followed the order;

$MgFe_2O_4$ (81.6 %) > Cu Fe_2O_4 (70.2%) > Ni Fe_2O_4 (51.6%) > C0 Fe_2O_4 (40.3 %) > Zn Fe_2O_4 (37.5%)

The catalyst was washed and dried after the reaction is over. It was used again five times for this condensation without any significant decrease in its activity. Thus, catalyst is recyclable. The results are reported in table-5.

Table -5. Reusability of magnesium ferrite

Used	**Yield(%)**
First	100.0
Second	98.4
Third	97.2
Fourth	96.3
Fifth	95.2

APPLICATION

The magnesium ferrite has been successfully used as nanocatalyst in driving Knoevenalgel condensation. It can be applied as catalyst to other organic reactions of synthetic importance.

CONCLUSION

The $MgFe_20_4$ nanoparticles with an average size of 82.47 nm were prepared via a hydrothermal procedure using Teflon lined autoclave. These nanoparticles were utilized as a catalyst in the presence of potassium hydroxide for the Benzyl- benzilic acid rearrangement reaction of benzyl and ethyl alcohol. This approach has several significant advantages such as good yield in lesser time. This technique is simple, and the catalyst may be reused more than five times without any major lose in its catalytic activity. Thus, magnesium ferrite can be used as benign catalysts for Benzil-benzilic acid rearrangement reactions.

REFERENCES

1. M. Odagi, T. Matoba, K. Hosoya, and K. Nagasawa, Enantioselective total synthesis of (+)-stephadiamine through bioinspired aza-benzilic acid type rearrangement. J. Am. Chem. Soc., **143**(7), 2699-2704 (2021).

2. H. Wu, Q. Wang, and J. Zhu, Catalytic enantioselective benzilic ester rearrangement. Angew. Chemie Int. Edi., **59**(18), 7261-7265 (2020).

3. M. Xiao, W. Wu, L. Wei, X. Jin, X. Yao, and Z. Xie, Total synthesis of (−)-isatisine A via a biomimetic benzilic acid rearrangement. Tetrahedron, **71**(22), 3705-3714 (2015).

4. M. Schwiderski and A. Kruse, Catalytic effect of aluminium chloride on the example of the conversion of sugar model compounds. J. Mol. Catal. A Chem., **402**, 64-70 (2015).

5. K. C. Babu Naidu, and W. Madhuri, Bull. Mater. Sci., 40 417-425 (2017). https://doi.org/10.1007/s12034-017-1374-4.