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Use of some metalferrites as catalyst in Schotten-Baumann reaction

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ABSTRACT

Zinc ferrite was used to catalyse the Schotten-Baumann reaction of benzoyl chloride and aniline in the presence of sodium hydroxide. Zinc ferrite was prepared by hydrothermal process. Other magnetic ferrites (Where M=Ni, Co, Zn, and Mg) were also prepared. 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 Zinc ferrite was found to have 6.62 nm and these are irregular in shape. The product was confirmed by m.p. and m.m.p. It was found that the yield of the product (benzanidide) in the presence of Zinc ferrite was 61.3%, which is almost 2.4 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:
$ZnFe_2O_4$ (61.3%) > Ni Fe_2O_4 (51.7%) > Co Fe_2O_4 (44.5 %) > $MgFe_2O_4$ (38.0 %) > Cu Fe_2O_4 (26.2%)

1. Introduction

Magosso et al. [1] synthesized turt-butyl peroxy-2-methyl hexahonate (TBPEH) in the presence of a strong base, and used in the Schotten–Baumann reaction from 2-ethylhexanoyl chloride and *tert*-butyl hydroperoxide. The kinetics of the synthesis of *tert*-butyl peroxy-2-ethylhexanoate was investigated in a capillary microreactor. It was reported that phase transfer catalyst (PTC) increased the peroxyesterification rate without affecting the rate of hydrolysis. The best performance was given by quaternary ammonium salt with longer alkyl chains, where peroxyesterification becomes 25 times faster. The increase in rate was found proportional to the amount of PTC.

Rong et al. [2] developed a vapor-phase grafting strategy for postsynthetic modification of metal–organic frameworks (MOFs) via Schotten–Baumann reaction between acyl chloride and amino groups and hydrolysis of –COCl. It was reported that carboxylated MOFs can be prepared on simple exposure in vaporized acyl chloride molecules and immersion in water. It was revealed that modified MOFs maintained crystalline structures as well as porosities and it exhibited improved performance for removal of fluoride.

Megías-Sayago et al. [3] invesgated catalytic activity of Au/Al_2O_3, which was evaluated in the selective oxidation of 5-hydroxymethylfurfural (HMF) prepared by the direct anionic exchange (DAE) method. This reaction was carried out and molecular oxygen was used as an oxidant. They observed the effect of the HMF/NaOH ratio and reaction time on yield of product and their distribution. It was reported that high activity and selectivity could be achieved under mild conditions, and 2,5-furandicarboxylic acid (FDCA) production 99% after 4 h using 4 equivalents of NaOH at 70°C. It was found that catalyst stability was confirmed by repeating the reaction for five times.

Begum et al. [4] synthesized amide derivatives of *N*-phthaloylglycine via under Schotten Baumann reaction. As-synthesized compounds were evaluated for their *in-vitro* Butyrylcholinesterase (BChE) and inhibition and it was observed and all exhibited good activity against this enzyme. One of the compound 4a was found to be most potent with $IC_{50} = 6.5 \pm 0.1$ as compared with the reference compound galantamine ($IC_{50} = 6.6 \pm 0.00038$). It was suggested that this compound can be employed a lead compound against Alzheimer's disease.

The N-acylated amino acids are commonly used as surfactants in some cosmetics and household formulations and these are produced on such industrial using Schotten-Baumann reaction. Heiner growing demand for greener processes as a potential alternative for selective enzymatic synthesis in more eco-friendly

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conditions. Bourkaib et al. [5] used aminoacylases from *Streptomyces ambofaciens* for selectivel catalysis aminoacid acylation reaction using fatty acids in aqueous medium. It was represent 9 amino acids were acylated preferentially by *S. ambofaciens* aminoacylases in the following order: Lysine > Arginine > Leucine > Methionine > Phenylalanine > Valine > Cysteine > Isoleucine > Threonine.
It was also observed that length of fatty acid affected the conversion yield. It was interring to note that addition of cobalt led to a more than six-fold increase in reaction rate.

Zhao et al. [6] synthesized natural α-amino acid derivative *N*-dodecanoyl leucinate via Schotten–Baumann reaction on alkali treatment. It was then applied to the dispersion of arc-discharged single-walled carbon nanotubes (SWCNTs). An effective individualization and selective dispersion of SWCNTs. Was confirmed. It was suggested that the formation of a charge transfer complex between SWCNTs and dispersants was responsible for the effective individualization of SWNTs. It was also revealed that charge transfer from dispersants to SWCNTs. or from vice-versa is crucial for selective dispersion of semiconducting or metallic SWCNTs.

Ballarini [7] synthesized silsesquioxanes-based (SQ) porous polymers via two main steps: (I) synthesis of the precursors, and (II) polymerization between the organic and inorganic part. The sol-gel process was used for the synthesizing of SQs, but 5,5',6,6'- tetrahydroxy -3,3,3',3'-tetramethyl-1,1'- spirobisindane (TTSBI), was synthesised via a cyclization step. These followon cross-linking reactions were based on Schotten-Baumann reaction and Michael addition. They obtained three hybrids as 0.01TTSBI, T8TTSBI and T8SEBCL. It was revealed that these were used as adsorbents in adsorption of dyes. Out of these 0.0TTSBI was found to be most versatile, to dyes and the heavy metal ions.

Deepa and Rajkumar et al. [8] synthesized luminol based methacrylamide monomer (LUME) was using a simple Schotten-Baumann type reaction. They used methacryloyl chloride and luminolas the reactants. They copolymerized LUME with hydroxyethyl methacrylate (HEMA) using Single electron transfer-living radical polymerization. It was reported that luminol functionalized homo (PML) and copolymer (PHL) had excellent solubility in basic medium and also in polar solvents such as dimethyl formamide and dimethyl sulfoxide. It was found that 1 μM of peroxide can be sensed with a very dilute solution of PML (1.8 x 10^{-11}M) and PHL (2 x 10^{-8}M). As-prepared chemiluminescent polymethacrylamides can also be used for peroxide sensing in live cells.

Bamane et al. [9] developed an efficient synthetic route to polyhydroquinolines via four component condensation reactions of dimedone, aldehydes, and ammonium acetate, ethyl acetoacetate and in the presence of guanidine hydrochloride (catalyst) in ethanol at room temperature. They carbohydrazide derivatives were synthesized using Schotten-Baumann reaction. Added advantages of this protocol are simple work-up procedure, eco-friendly nature, non-toxic catalyst, inexpensive, short reaction times and excellent yields of product.

A synthetic route was developed and scaled-up for tasisulam sodium (5-bromo-thiophene-2-sulfonic acid 2,4-dichlorobenzoylamide sodium salt (taissulam) via a continuous Schotten–Baumann reaction by White et al. [10]. It was reported that as-developed Schotten–Baumann conditions has only fewer unit operations than the conventional batch process through direct formation of the final sodium salt from acid chloride and sulfonamide without isolating free acyl sulfonamide.

2. Experimental

Synthesis of zinc ferrite nanoparticles

Hydrothermal method was used to prepare zinc ferrite using a similar method as Naidu and Madhuri [11]. Zinc nitrate [Zn $(NO_3)_2$] and ferric nitrate [Fe $(NO_3)_3.9H_2O$] were used as precursor of zinc and iron, respectively. A Teflon coated autoclave was used for this purpose. Zinc 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 drop wise into the solution in 1:4 ratios till the pH was maintained at 11.The mixture was vigorously stirred for 2h and transferred into Teflon coated stainless steel autoclave and sealed. Then autoclave was heated at 150℃ for around 48h. 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.

Schotten-Baumann reaction catalyzed by zinc ferrite

The 3.5 mL of benzoyl chloride was added after taking 2.5 mL of aniline 2.5 g of sodium hydroxide pellets and 0.10 g zinc ferrite in a conical flask. It was shaken for ten min. The product was filtered as a white powder. It was washed and then dried. It was recrystallized with hot alcohol. It was separated using a heated Buchner funnel.

$$C_6H_5NH_2 + C_6H_5COCl + NaOH \xrightarrow{\text{Zn-ferrite}} C_6H_5NHCOC_6H_5 + NaCl + H_2O \quad \text{Yield (61.3\%)}$$

3. Results and discussion

Field Emission Scanning Electron Microscopy (FESEM)

The as-prepared copper ferrite particles were characterized by scanning electron microscope (SEM) on JSM-6100 (JEOL) with a digital image processor. The FSEM images have been given in Fig.1. The morphology of zinc ferrite was found to be irregular shaped.

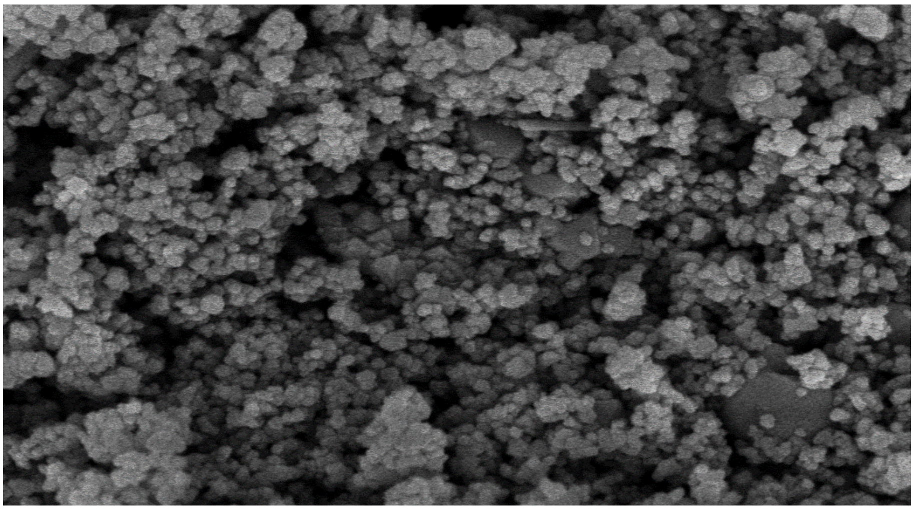

Fig. 1: FESEM image of zinc ferrite

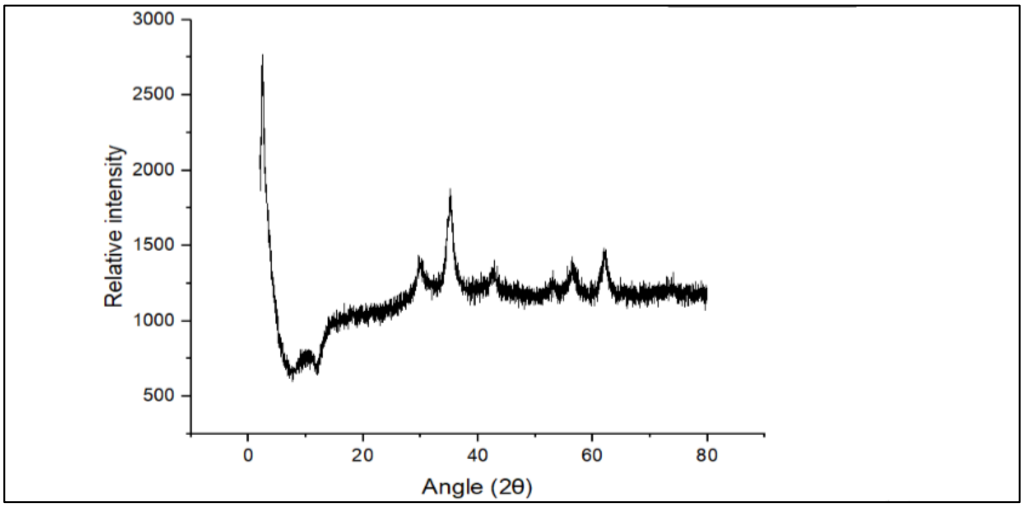

Fig. 2: Powder XRD pattern of zinc ferrite

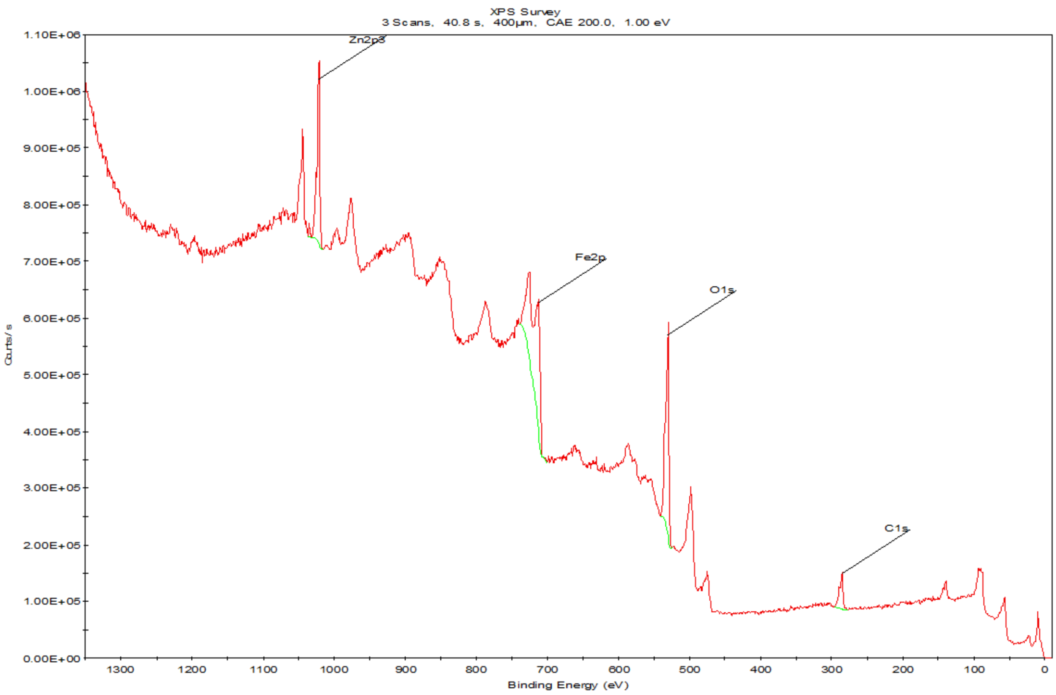

Fig - 3: XPS Analysis of zinc ferrite

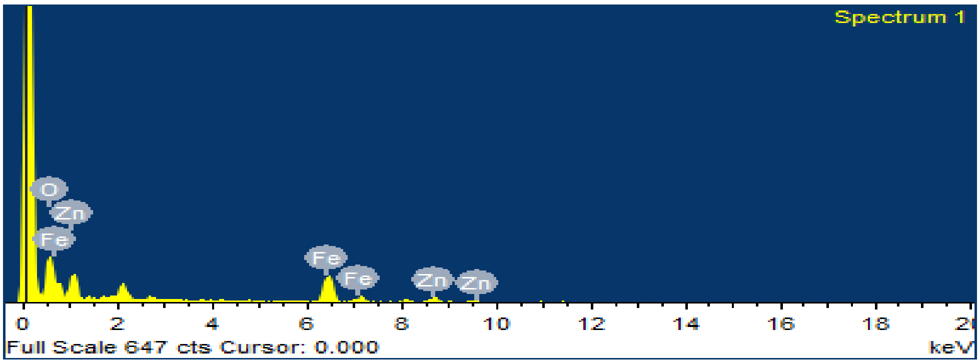

Fig- 4: EDX analysis of zinc ferrite

X-Ray Diffraction (XRD)

The crystalline nature of the synthesized zinc ferrite sample was observed by X-Ray diffraction pattern. A X' Pert Pro XRD equipped with X' Celerator solid – state detector was used and result are reported in Fig. 2. The average particle size of particles was calculated by Debye-Scherer equation and it was found to be in quantum dots size (6.62 nm).

X-Ray Photoelectron Spectroscopy(XPS)

X-Ray photoelectron spectral analysis was also carried out using a Thermo K-alpha + X-ray spectrometer. Contact angle measurement was carried out using a KRUSS drop shape analyzer. It gives Zn, Fe and O in $2p^3$, 2p and 1s states, respectively.

Energy-Dispersive X-Ray Spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy with JSM 7600 F (Jeol) showedpeaks for Fe, Zn and O, only which indicates that zinc ferrite is in pure state and it does not contain any impurity.

Fourier Transform Infrared Spectrum

FTIR Spectrometer RX-I was used to record IR spectrum of the product. The spectrum is gives in Fig. 5.

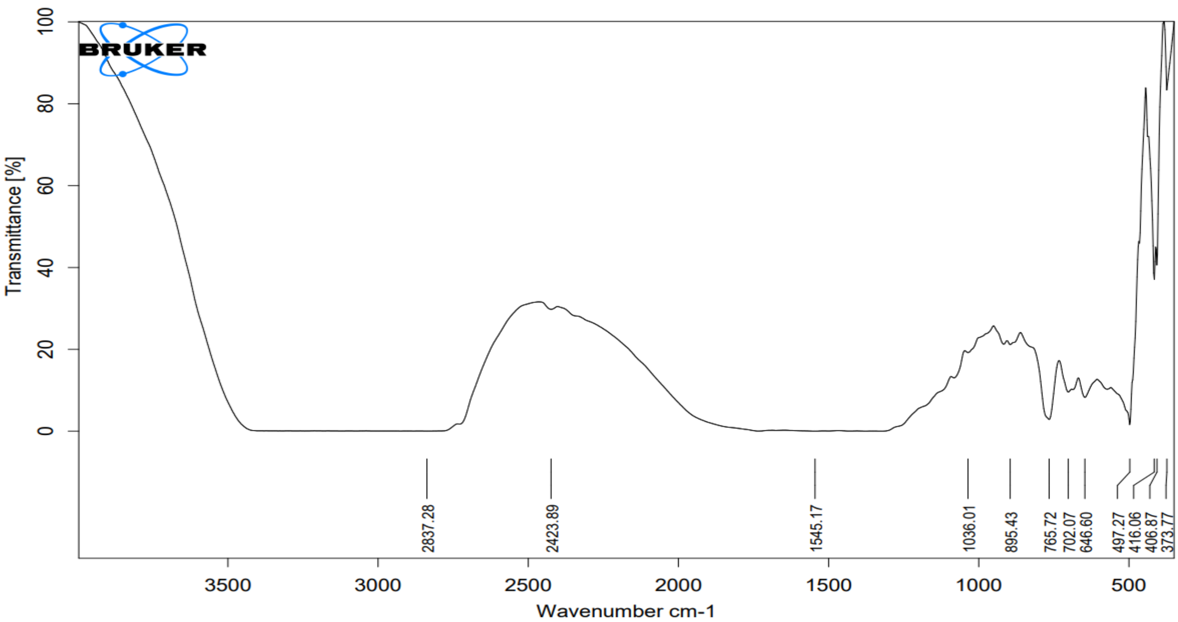

Fig- 5: FT- IR Spectrum of product

There is a broad band from 2837-3500 cm^{-1} which may be due to C- H vibrations in aromatic system. A band at 2423 cm^{-1} may be assigned to –NH stretching vibration. The presence of bands at 1545 cm^{-1} may be attributed to C=C stretching vibration. The C- H in-plane bending vibration is indicated by a band at 1036 cm^{-1} while C=O and C-C in-plane bending vibrations were observed at 895-765 cm^{-1}, respectively. All these bands supported that the product of reaction is benzanilide.

Fourier Transform Nuclear magnetic Resonance Spectrum

FT-NMR spectrometer model Advance-II (Bruker) (400 MHz) was used to record NMR spectrum of the product. The spectrum is given in Fig .6.

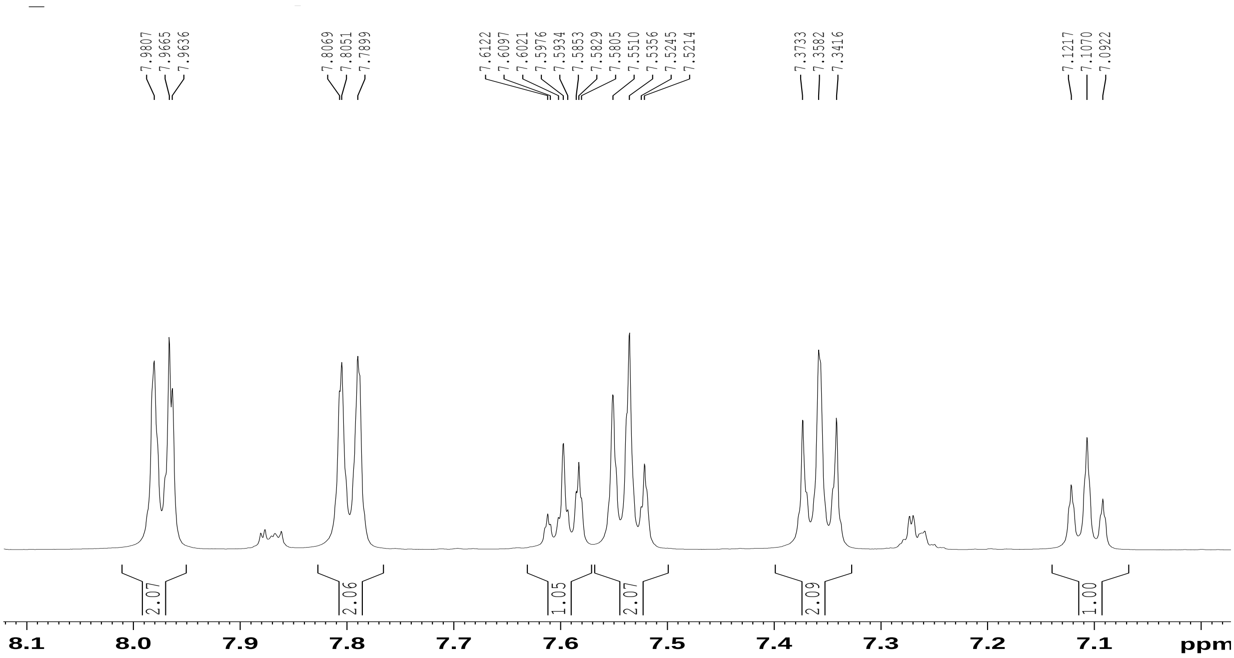

Fig -6: FT- NMR Spectrum of product

NMR spectrum of the product indicated some interesting features like pairs of doublet, triplet and multiplets. Two triplets at 7.0-7.1 δ and 7.58- 7.61 δ may be assigned to o- aromatic protons in two benzene ring. Two more triplets at 7.34-7.37 δ and 7.5- 7.55 δ may be attributed m- protons to –NH and –CO groups, respectively. There are two more triplet at 7.78-7.80 δ and 7.96-7.98 δ. These may be attributed to o- aromatic protons.

On the basis of FTIR and NMR results, it was confirmed that the product was benzanilide. It was also confirm by its m.p. and m.m.p.

Comparitive study of Schotten-Baumann reaction

Different factors were varied to achieve optimal conditions such as amount of aniline, catalyst, sodium hydroxide, and benzoyl chloride.

The effect of aniline was observed in the range of 2.0 - 3.5 mL. The results are shown in Table -1

Table-1 Effect of aniline

Aniline (mL)	Sodium hydroxide (g)	Benzoyl chloride (mL)	Zinc ferrite (g)	Yield (%)
2.0	2.5	3.5	0.10	20.6
2.5	2.5	3.5	0.10	45.0
2.5	2.5	3.5	0.10	61.3
3.0	2.5	3.5	0.10	44.8
3.0	2.5	3.5	0.10	28.7
3.5	2.5	3.5	0.10	18.1

It was observed that as the amount of aniline was increased keeping all other parameters constant, then the yield increases up to 2.5 mL of aniline and then it showed a declining behavior above 2.5 mL. It may be due to the fact that 2.5 mL is the required amount of aniline in this reaction above which it remains unreacted.

The effect of sodium hydroxide was observed in the range of 2.0–3.2 g. The results are shown in Table-2

Table-2 Effect of sodium hydroxide

Aniline (mL)	Sodium hydroxide (g)	Benzoyl chloride (mL)	Zinc ferrite (g)	Yield (%)
2.5	2.0	3.5	0.10	20.8

2.5	2.3	3.5	1.17	47.4
2.5	2.5	3.5	0.10	61.3
2.5	2.8	3.5	0.10	50.0
2.5	3.0	3.5	0.10	39.1
2.5	3.2	3.5	0.10	20.6

It was found that when the amount of sodium hydroxide was increased, the yield of product increases up to 2.5 g of sodium hydroxide and then it declined on further increasing its amount. It may due to the fact that the 2.5 g is the required amount of sodium hydroxide, above which it remains unreacted.

The effect of benzoyl chloride was observed in the range of 3.0-4.2 mL. The results are shown in Table-3

Table-3 Effect of benzoyl chloride

Aniline (mL)	Sodium hydroxide (g)	Benzoyl chloride (mL)	Zinc ferrite (g)	Yield (%)
2.5	2.5	3.0	0.10	20.5
2.5	2.5	3.2	0.10	44.2
2.5	2.5	3.5	0.10	61.3
2.5	2.5	3.7	0.10	44.3
2.5	2.5	4.0	0.10	36.9
2.5	2.5	4.2	0.10	28.4

It was found that when the amount of benzoyl chloride was increased, then the yield of product increases up to 3.5 mL of benzoyl chloride and then it declined on further increasing its amount. It may due to the fact that the 3.5 mL is the required amount of benzoyl chloride, above which it remains unreacted.

The effect of zinc ferrite was observed in the range of 0.052 – 0.01 g. The results are shown in Table-4.

Table-4 Effect of zinc ferrite

Aniline (mL)	Sodium hydroxide (g)	Benzoyl chloride (mL)	Zinc ferrite (g)	Yield (%)
2.5	2.5	3.5	0.07	29.07
2.5	2.5	3.5	0.08	33.3
2.5	2.5	3.5	0.09	50.2
2.5	2.5	3.5	0.10	61.3
2.5	2.5	3.5	0.12	41.7
2.5	2.5	3.5	0.13	24.2

It was found that when the amount of zinc ferrite was increased, then the yield of product increases up to 0.010 g of zinc ferrite and then it declined on further increasing its amount. 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 benzanilide could be obtained under the following optimum conditions:

Aniline = 2.5 mL, Sodium hydroxide = 2.5 g, Benzoyl chloride = 3.5 mL, Zinc ferrite = 0.1 g

A comparative study was also carried out to compare the efficacy of different metal ferrites for Schotten–Baumann reaction which followed the order:

$ZnFe_2O_4$ (61.3%) > Ni Fe_2O_4 (51.7%) >Co Fe_2O_4 (44.5 %) > $MgFe_2O_4$ (38.0 %) >Cu Fe_2O_4 (26.2%)

4. Conclusion

The $ZnFe_2O_4$ nanoparticles were prepared with an average size of 6.62nm via hydrothermal process in a Teflon coated autoclave. These nanoparticles were used as catalyst in presence of sodium hypo chlorite solution for Schotten-Baumann reaction of aniline and benzoyl chloride under mild conditions. Some of the important advantages of this method are high yield, less time, and mild reaction conditions. This process is easy. The catalyst can be reused 5-6 times without any significant loss of catalytic activity. This catalystis environment friendly in nature.

Disclaimer

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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