

## NANO CATALYTIC ORGANIC SYNTHESIS

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### ABSTRACT

Nano particles are sometimes characterised as materials with one or more dimensions of smaller than 100 nm and, as a result, have unique properties distinct from their bulk equivalents or atomic / molecular constituents. Because of their small size and thus high surface to volume ratio, nano particle materials have recently been the subject of active research. The subject of nano science has grown at an exponential rate year after year due to novel synthetic methods and the availability of new equipment. characterization. The 2016 Nobel Prizes in Physics and Chemistry highlight the development and importance of path breaking discoveries in nano materials for the future and benefit of the mankind.

Nano catalysis aids in the expansion of new catalysts with high selectivity, constancy, and activity. These properties are readily gotten by adjusting the morphology, shape, size, composition, electrical construction, and thermal and chemical constancy of the specific nanomaterial. Although nano catalysts have various benefits over traditional catalyst systems, isolating and recovering these tiny nano catalysts from the reaction mixture is difficult. To address this issue, magnetic nanoparticles have emerged as a possible alternative; their insoluble and paramagnetic character allows for simple and fast parting of the catalysts from the response combination using an exterior magnet.

One of the most important features of heterogeneous catalysis appears to be the high catalytic activity of transition metal oxides. Ferrites, which are a class of magnetic oxide components that contain iron oxide as a major component has got numerous applications in electronics and electronic applications and communication devices. The magnetic properties and the strong acidic and basic sites of these ferrites paved way for developing new applications in catalysis.

### **Introduction**

The utilisation of nano Copper-Cobalt ferrite material as attractively divisible and refillable heterogeneous catalysts for the production of, -unsaturated ketones via the allylation of acid chlorides with allyl bromides is described. The response of allyl halides with different acid chlorides is carried out at room temperature in tetrahydrofuran (THF) utilising ultrasonication in the presence of nano ferrite particles. The current technology is ecologically friendly and produces excellent results. Using a powerful magnet, the catalyst is removed from the reaction media and reused numerous times without losing much catalytic activity. The reaction mechanism and product characterisation are provided.

Since of the rich photochemistry of olefins and ketones,-unsaturated ketones are the most widely studied photochemical systems. It has been discovered that combining both groups in the same molecule results in a variety of fascinating reactions [1]. The factors that influence their competition are not completely understood. Because of their widespread use in organic synthesis, the mixture of these moieties is continuously enticing to chemists.

### **3.0 Background of the Work**

The great proclivity of,-unsaturated ketones for prototropic rearrangement [2-3], which results in conjugated,-unsaturated ketones, complicates the synthesis of this class of compounds. The synthetic organic chemist has numerous techniques for constructing,-unsaturated ketones, although many of these procedures yield isomeric mixes of, and, unsaturated ketones [4-6]. Although the use of change metal such as nickel and rhodium has been documented, these approaches have low regioselectivity [7-8].

During the development of new catalysts, a new method was developed in which a

series of refillable nano copper-cobalt ferrite catalysts were used for the allylation of acid chlorides at room temperature in tetrahydrofuran (THF) using ultrasonication method, which gives high yields at smaller reaction times (0.5-1.0 hours) and without the formation of isomeric products. The entire synthetic approach is shown in **Scheme 3.1**.

### 3.1 Experimental

#### 3.1.1 General procedure for one pot synthesis of $\beta,\gamma$ -unsaturated ketones

A combination of allyl bromide (1 mmol) or cinnamyl chloride (1 mmol) in THF (5 mL) with stirring and 0.1 mol% (250 mg) copper-cobalt ferrite ( $\text{Cu}_0.5\text{Co}_0.5\text{Fe}_2\text{O}_4$ ) was prepared in a 25 mL beaker. To that, benzoyl chloride (1 mmol) in THF (10 mL) was added, and the response combination was put in an ultrasonication tray and sonicated at room temperature for 0.5-1.0 hours (as displayed in Table 3.3). TLC was used to monitor the development of the reaction, which used mobile phase in a 2:1 ratio (hexane, ethyl acetate). TLC confirmed that the reaction was complete when the catalyst was removed using a sturdy magnet at the lowest of the beaker and the contents were transferred to another container. The catalyst was rinsed with 5 mL of THF to prepare it for the products. To get the end products of  $\beta,\gamma$ -unsaturated ketones, the flush was withdrawn under summary weight and the products recrystallized with ethanol.

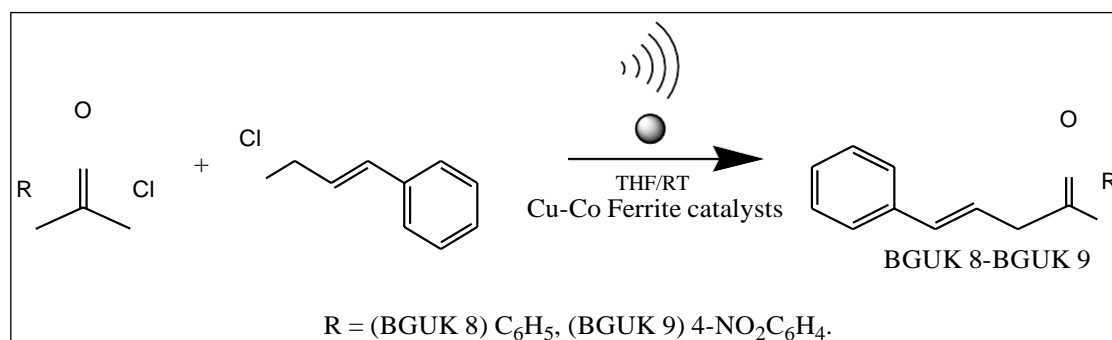
After obtaining the product, the catalyst was dehydrated, separated, and eroded with diethyl ether, ethyl acetate, and alcohol. The catalyst was then dried and microwave irradiated to activate it, and the healthier catalyst was recycled for a few more cycles. The FT-IR spectra of the products also revealed that there was no leaching of catalyst in the product.

### 3.2 Results and Discussion

#### 3.2.1 Effect of Cu-Co ferrite catalyst on the synthesis of $\beta,\gamma$ -unsaturated ketones

One-pot synthesis of substituted  $\beta,\gamma$ -unsaturated Ketones was carried over different spinel systems under study at a THF/RT where a mixture of allyl bromide (1 mmol) or cinnamyl chloride (1 mmol) and benzoyl chloride (1 mmol) were ultrasonicated in ethanol as shown in **Scheme 3.1**. The yield of  $\beta,\gamma$ -unsaturated Ketones formation with variation in copper-cobalt ratio is presented in **Table 3.1**.

The results with allyl bromide have been extended with cinnamyl chloride. The synthetic route is obtainable in **Scheme 3.2**. The reaction was carried out under enhanced circumstances. The consequences are listed in **Table 3.3**.



### Scheme 3.2 Synthesis of $\beta,\gamma$ -unsaturated ketones using cinnamyl chloride

#### 3.1 Effect of metal ratio in the catalyst and method on reaction time and yield %

S.No	Catalyst	Method	Time (min)	Yield (%)
1	CuFe <sub>2</sub> O <sub>4</sub>	Reflux	110	80
		Ultrasonication	90	80
2	Cu <sub>0.75</sub> Co <sub>0.25</sub> Fe <sub>2</sub> O <sub>4</sub>	Reflux	60	82
		Ultrasonication	30	85
3	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	Reflux	60	85
		Ultrasonication	30	90
4	Cu <sub>0.25</sub> Co <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub>	Reflux	60	85
		Ultrasonication	30	90
5	CoFe <sub>2</sub> O <sub>4</sub>	Reflux	60	85
		Ultrasonication	30	95

It is observed from **Table 3.1** that cobalt was swapped for Copper ferrites have

demonstrated effective yields for the production of, - unsaturated ketones when ultrasonicated. When these reactions were compared to those with copper ferrite at room temperature [42], the reaction time was 180 minute. In this situation, the mutual impact of the catalyst and ultrasonication dramatically decreased the reaction time, which is a major contribution from this work.

### 3.2.2 Comparison of present catalysts with other reported catalysts

As mentioned above, several catalyst have been reported for the mixture of substituted  $\beta,\gamma$ -unsaturated ketones by the mixing of Allyl bromide or cinnamyl chloride and benzoyl chloride in THF/RT under ultrasonication in presence of various catalysts have been presented in **Table 3.2**. It is further observed from the literature that the synthesis of substituted  $\beta,\gamma$ -unsaturated ketones with substituted benzoyl chlorides in presence of nano copper-cobalt ferrite has not been reported earlier

**Table 3.2 Comparative study of various catalysts on reaction temperature, time and yield**

S.No	Catalyst	Method	Temp ( <sup>o</sup> C)	Time (hours)	Ref.
1	Bis (cyclooctadiene) Nickel(0)	Reflux	RT	15.0	40
2	Zn	Reflux	RT	3.0	37
3	Cd	Reflux	RT	3.0	39
4	In	Reflux	RT	3.0	38
5	BuSnCl <sub>2</sub> + Additive	Reflux	RT	2.0	41
6	CuFe <sub>2</sub> O <sub>4</sub>	Reflux	RT	1.5	42
7	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	Reflux	RT	1.0	-
8	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	Ultrasonication	RT	0.5	-

### 3.2.3 Plausible mechanism for the catalytic activity of the reaction

A viable explanation for the reaction's catalytic activity had been provided. It follows an acid catalysed route, as predicted by the mechanism (Scheme 3.3).

The production of allyl Ketone was not detected when the response was carried out with aliphatic long chain acid chlorides. It seems that neither electrical nor steric possessions play a significant role in the acylation of allyl halides by nano catalyst. All acylation processes occur via allylic rearrangement [27, 54-56], removing the double bond from the conjugation. The in situ mechanism of electrophilic assault of nano ferrite at the carbon atom of the allylic moiety will respond with the acyl halides to produce the title compound. FT-IR and  $^1\text{H}$  NMR spectrum investigations demonstrate the production of stable allyl ketone. The attendance of a steady olefinic bond is confirmed by the chemical shift at 4.5-6.0 as doublet of doublet in  $^1\text{H}$  NMR spectra. This implies that allylation occurs without any prototropic transformation at carbonyl carbon.

### 3.2.4 Characterisation of $\beta,\gamma$ -unsaturated ketones

FT-IR peaks at about 1695  $\text{cm}^{-1}$  suggesting Ketone C=O functional group, 1620  $\text{cm}^{-1}$  indicating C=C functional groups current in the chemical classified the reaction products substituted, -unsaturated ketones.

The chemical shift at 4.5-6.0 (dd, 2H) as doublet of doublet, peak at 3.0-3.5 (d, 2H) verifies the existence of double bond, and a multiplet at 7.0-8.8 settles the attendance of aromatic protons in the  $^1\text{H}$  NMR spectra.

The mass spectrum reveals the molecule's molecular weight as well as the  $\text{M}^+$  peak, while the fragments provide information on the daughter ions.

### 3.3 Process Optimization of reaction conditions on synthesis of $\beta,\gamma$ -unsaturated Ketone derivatives

Influence of Reaction Conditions i.e. effect of solvent, reaction time are studied in terms of percentage yield of the products formed for process optimization when THF solutions of Benzoyl chloride reacted with Allyl bromide or cinnamyl chloride in presence of copper-cobalt ferrite catalyst.

#### 3.3.1 Effect of solvent on synthesis of $\beta,\gamma$ -unsaturated ketones derivatives

The analysis of the process's reaction medium found that solvents played a key part in the reaction under inquiry. Table 3.4 summarises the findings. Various solvents such as diethyl ether, tetrahydrofuran, dichloromethane, and acetonitrile were tested for this process. The reaction was found to be more efficient in tetrahydrofuran than in the other solvents tested.

**Table 3.4 Effect of solvent on the reaction time and yield %**

S.No	Catalyst	Solvent	Time (hours)	Yield (%)
1	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	THF	0.5	94
2	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	2	80
3	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	Dichloromethane	5	64
4	Cu <sub>0.5</sub> Co <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	MeCN	10	Trace

### 3.4 Recycling of the Catalysts

The reusability of catalysts is a fundamental challenge in heterogeneous catalysis. The catalyst's recovery and reusability were examined. Catalyst recycling was accomplished by magnetically attaching the catalyst to the bottom of the flask with a robust magnet, then removing the solution with a pipette, washing the solid twice with acetone and ethyl alcohol, and introducing the renewed substrate dissolved in the same flush into the flask, allowing the reaction to proceed for the next run. The catalyst was reused five times in a row with no discernible loss of catalytic activity. As a result, they may be readily and nearly totally separated by an external magnet, which is extremely beneficial for a heterogeneous catalyst.

### CONCLUSIONS

The primary goal of this research is to synthesise and characterise micro crystalline copper-cobalt ferrites, as well as to investigate their catalytic use in the synthesis of a novel class of organic compounds via one-pot multicomponent synthesis employing greener methodologies. The catalysts were created using a soft chemical technique using citrate sol-gel methods. Pure nanocrystalline copper-cobalt ferrites having the formula  $Cu_xCo_{1-x}Fe_2O_4$  ( $x=0, 0.25, 0.5, 0.75, \text{ and } 1$ ). The catalysts were identified

and employed in the study as magnetically separable nano catalysts. This approach provided a high yield while also ensuring full uniformity. As a result, this procedure might be scaled up.

**The objectives of the study are:**

1. To use the citrate sol-gel technique to create nano spinel copper-cobalt ferrites with the formula  $Cu_xCo_{1-x}Fe_2O_4$  ( $x = 0, 0.25, 0.5, 0.75, \text{ and } 1$ ).
2. To evaluate the structure, shape, and size of the generated nano ferrites, characterise them using FT-IR, XRD, SEM, EDX, TEM, and BET surface area methods.
3. To use the synthesised ferrites as heterogeneous magnetically separable catalysts and to optimise the process for the one-pot synthesis of, -unsaturated ketones, 3,4-dihydro-pyrimidine-2(1H)-ones/thiones, -acetamido esters, and -acetamido ketones using ultrasonication, reflux, and microwave irradiation.
4. Use FT-IR,  $^1H$  NMR, and MASS spectrum analysis to characterise the structure of freshly synthesised heterocyclic compounds.
5. Research into the biological activities of newly synthesised heterocyclic chemicals.

In the light of the above objectives, nano particles of copper-cobalt ferrites with the general formula  $Cu_xCo_{1-x}Fe_2O_4$  have been manufactured by citrate sol-gel method. The FT-IR spectra show the absorption band around  $575\text{cm}^{-1}$  which is credited to the stretching vibrations of tetrahedral complexes. The band around  $410\text{ cm}^{-1}$  is attributed to the stretching vibrations of octahedral complexes. The XRD spectra reveal the average crystallite size to be in the range 30-40 nm and this is found to be in agreement with TEM results. The SEM micrographs show the appearance of a sponge like structure. The EDAX spectra confirm the presence of metallic compounds without impurities.

In the process of development of new catalysts, enhancing the reaction yields and reducing the reaction times for the reactions, a new method was developed in which a series of reusable nano copper-cobalt ferrite catalysts were used for the allylation of acid chlorides at room temperature in tetrahydrofuran (THF) using ultrasonication technique, which gives high yields at shorter reaction times (0.5-1.0 hours) and without the formation of isomeric products.

One-pot synthesis of substituted  $\beta,\gamma$ -unsaturated Ketones was carried over different



spinel systems under study at a THF/RT where a mixture of allyl bromide (1 mmol) or cinnamyl chloride (1 mmol) and benzoyl chloride (1 mmol) were ultrasonicated in ethanol as shown below. The yield of  $\beta,\gamma$ -

unsaturated Ketones formation with variation in copper-cobalt ratio is presented.

### References

- [1] Altavilla C and Ciliberto E 2010 Inorganic Nano particles Synthesis, Applications, *Perspectives Google eBook, CRC Press*.
- [2] Smit J and Wijn H P J 1959 *Philips Technical Library Eindhoven*. The Netherlands
- [3] Good enough J B and Loeb A L 1955 *Phys. Rev.* **98** 391
- [4] Harrison W F 1957 *Phys. Rev.* **106** 5 865-866
- [5] Koning Von U and Chol G 1968 *Appl. J. Cryst.* **1** 124-127
- [6] Hill R J, Craig J R and Gibbs G V 1979 *Phys. Chem. Miner.* **4** 317
- [7] Carta D, Casula M. F, Falqui A, Loche D, Mountjoy G, Sangregorio Cand Corrias A 2009 *J. Phys. Chem. C.* **113** 8606–8615
- [8] Song Q and John Zhang Z 2004 *J. Am. Chem. Soc.* **126** 19 6164–6168
- [9] Datta R K and Roy K 1961 *Nature.* **191** 169
- [10] Ka'roly L, Mathew T B, Koppa'ny Z, Ja'nos M, Violet S, Subhash P M, Bollapragada S R and La'szlo' G 2002 *Chem. Phys.* **4** 3530–3536
- [11] Sathya A, Guardia P, Brescia R, Silvestri N, Pugliese G, Nitti S, Manna L and Pellegrino T 2016 *Istituto Italiano di Chem. Mater.*, **28** 6 1769–1780
- [12] Miller A 1959 *Appl. J. Phys.* **30** 245
- [13] Courty P, Marcilly C, Delmon B, Jacobs P A and Poncelet Eds G 1976 *Stud. Surf. Sci. Catal.* **1** 119
- [14] Toledo-Antonio J A, Nava N, Mart'inez M and Bokhimi X 2002 *Applied Catalysis. A.* **234** 137–144
- [15] Debanjan G, Babita B and Sunkara V 2005 *Manoram. Journal of Molecular*

*Catalysis A.* **242** 26–31

- [16] Braga T P, Campos Sales B M, Pinheiro A N, Herrera W T, Baggio-Saitovitch B E and Valentini A 2011. DOI: 10.1039/c1cy00176
- [17] Deraz N M, Alarifi A and Shaban S A 2010 DOI:10.1016/j.jscs.2010.04.012
- [18] Xiangxin Y, Chundi C, Kenneth J K, Keith L H and Larry E E 2007 *Ind. Eng. Chem. Res.* **46** 14 4819–4823
- [19] Viswanathan B, Krishnamurthy K R and Sastri M V C 1979 *Res. Inst. Catalysis.* **27** 2 79-88
- [20] Romeijn F C 1953 *Philips Research Reports.* **18** 304
- [21] Bate G and Craik E D D J 1975 *Wiley Inter Science.* 703
- [22] Sharrock M P 1989 *IEEE Trans. Magn.* **25** 374
- [23] Haneda K and Morrish A H 1988 *Appl. J. Phys.* **63** 4258
- [24] Tailhades P, Villette C, Rousset A, Kulkarni G U, Kannan K P, Rao C NR and Lenglet M 1998 *Solid State Chem. J.* **141** 56
- [25] Ahn Y, Choi E J, Kim S and Ok H N 2001 *Mater. Lett.* **50** 47
- [26] Hanh N, Quy O K, Thuy N P, Tung L D and Spinu L 2003 *Physica B.* **327** 382
- [27] Chinnasamy C N, Senoue M, Jeyadevan B, Perales-Perez O, Shinoda Kand Tohji K 2003 *Colloid Interf. J. Sci.* **263** 80
- [28] Lelis M F F, Porto A O, Goncalves C M and Fabris J D 2004 *J. Magn. Mater.* **278** 263
- [29] Chae K P, Lee J, Kweon H S and Lee Y B 2004 *J. Magn. Mater.* **283** 103
- [30] Liu C, Zou B, Rondinone A J and Zhang Z J 2000 *J. Phys. Chem B.* **104**

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1141-5

[31] Zhen L, He K, Xu C Y and Shao W Z 2008 *J. Magn. Magn. Mater.* **320**

2672-5

[32] Kim D H, Nikles D E, Johnson D T and Brazel C S 2008 *J. Magn Magn Mater.*