iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 8 **Issue:** IV **Month of publication:** April 2020

DOI: http://doi.org/10.22214/ijraset.2020.4036

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
Volume 8 Issue IV Apr 2020- Available at www.ijraset.com

Studies on Eco-friendly Solid Acid Catalysts for the Synthesis of 4-Chloro, 4’-Hydroxy Benzophenone by Friedel-Crafts Acylation Reaction.

Milin Thakkar[1], Sanjay Sonawale[2]
[1, 2]Department of Chemistry, Kirti M. Doongursee college of Arts, Science and Commerce.

Abstract: 4-Chloro,4’-Hydroxybenzophenone is an essential intermediate for the synthesis of fenofibrate class of lipid lowering drugs and Poly Ether Ketone (PEK). A new method is developed for synthesizing 4-Chloro,4’-HydroxyBenzophenone from reaction of phenol with p-Chlorobenzotrichloride and p-Chlorobenzoylchloride in ethylene dichloride at different temperatures using K-10 clay Supported metal chloride solid catalysts. In the present study iron, zinc, aluminum, antimony, bismuth, and zirconium were used for their efficacy. 24 different catalysts were prepared and used as catalyst for the conversion with two different reagents. TheFe^{3+} supported on K-10 clay was found to yield 97% product. The method merits over conventional methods as it reduces the generation of hazardous waste, eco-friendly and simple in workup process and easy separation.

Keywords: 4-Chloro,4’-Hydroxy Benzophenone, solid acid catalysts, Montmorillonite K-10 clay, heterogeneous catalysts.

I. INTRODUCTION

4-Chloro,4’-Hydroxy Benzophenone is one of the fundamental intermediates in chemical industry. It is synthesized by several methods by reaction of phenol with different acylating agents such p-chlorobenzoic acid[1], p-chlorobenzoylchloride[2], p-chlorobenzotrichloride[3], etc ., in presence of catalysts such as Hydrofluoric acid, polyphosphoric acid and anhydrous aluminium choride. These catalysts are highly corrosive and polluting therefore, a new process for the synthesis of 4-Chloro,4’-HydroxyBenzophenone by Friedel-Crafts acylation reaction using the eco-compatible catalyst is desirable. For these reactions the setting up of more eco-compatible Friedel-Crafts acylation reaction has become a fundamental goal of the revolution that has spread in all the fields of synthetic chemistry through a revision of preparation methods mainly based on exploitation of new and increasingly efficient catalysts.

Solid heterogeneous catalysts can be separated easily from the reaction mixture and reused; they are generally not corrosive. Different heterogeneous catalysts have been utilized for the Friedel-Crafts acylation reactions. These includes Zeolites, Acid treated metal oxides, Heteropolyacids, Perfluorinated resin sulfonic acids and clays. Catalysts help the synthetic chemists in a big way in achieving many of these goals and making processes greener.

A catalyst can be homogeneous or heterogeneous. In homogeneous catalysis the reactant and the catalyst are in the same phase; while in heterogeneous catalysis they are in the different phases. Considering complementary properties of homogeneous and heterogeneous catalysts efforts are being made to prepare a new class of catalysts called Heterogenized Homogeneous Catalysts. The central concept in this catalyst is fixing of the active catalytic species on some insoluble solid material. These heterogenized homogeneous species have attracted wide attention not only to the advantages they share with homogeneous catalysts in general but also due to the fact that depends upon the support used, the catalytic activity of the species can be modified to a great extent. For example, using a classical homogeneous inorganic catalyst, like a Lewis acid, a variety of mechanistically compatible heterogenized catalysts can be prepared by merely changing the support. A variety of inorganic reagents can thus be immobilized on supports like clay. In recent years, organic chemists have paid considerable attention to organic reactions effected by reagents immobilized on finely divided solids, for which the term supported reagent has been coined[4-6]. The term support reagent refers to reagents obtained by the adsorption on dispersion over or intercalation in an insoluble support material of a chemical reagent. These may be replaced into two groups depending upon the nature of the support[7]. A number of clays supported reagents have recently been in the limelight and a lot of work is currently focused on the use of clays and montmorillonte K10, K10 in particular, as supports. Clayzic ($ZnCl_2$ – K10)[8], Clayfen (Iron(III) Nitrate- K10)[9], Claycop (copper chloride- K10)[10] are some of the significant heterogenized versions of homogeneous catalysts and which have been advocated largely in some of the important organic reactions such as Friedel-Crafts alkylation[11], acylation[12], oxidation[13], nitrations[14], etc. The use of a number of supports such as silica, alumina, graphite, carbon, montmorillonite, zeolites, kieselguhr, etc. has been reviewed[15-17].

Montmorillonite is the most widely used clay minerals, which is used as catalyst and catalyst support in organic reactions. The surface acidity of Montmorillonite is one of its remarkable features. Clay minerals with a high cation-exchange capacity (e.g. Montmorillonite) derive most of their Lewis acidity from the interlayer cations. Clays has surface acidity. Both, Lewis and Bronsted acidic sites are present in the clays. Clays can be modified by various methods, such as acid treatment, calcination, ion-exchange, impregnation of metallic salts on the surface and pillaring.

Solid catalysts are being employed for the design of benign synthetic process to minimize pollution. Montmorillonite K10 clay catalyst in its various forms has been widely studied. Metal ion treated K10 catalysts prepared by ion exchange (K10-MOA) and impregnation of metal salts in organic solvents (K10-MOO) at two different temperatures 120 ^{o}C and 550 ^{o}C are employed for various Friedel-Crafts alkylation and acylation reactions, Diels-Alder reaction, Ene reactions, etc. We herein, have prepared modified catalysts by two different methods namely 1. Ion exchange Method and 2. Impregnation Method with 6 different Lewis acid metal chlorides namely $AlCl_3$, $FeCl_3$, $SbCl_3$, $ZnCl_2$, $ZrCl_4$ and $BiCl_3$ and thermally calcined at 120 ^{o}C and 550 ^{o}C respectively and used them for the synthesis of 4-Chloro,4'-Hydroxy Benzophenone.

The primary objective of our work was prepare K10-MOO 120, K10-MOO 550, K10-MOA 120 and K10-MOA 550 montmorillonite K10 treated catalysts, were M = Fe^{3+}, Al^{3+}, Zn^{2+}, Sb^{3+}, Zr^{4+} and Bi^{3+}. Then, to investigate the catalytic activity of thus prepared catalysts to synthesize 4-Chloro,4'-HydroxyBenzophenone by Friedel-Crafts acylation of phenol with P-chlorobenzotrichloride and P- chlorobenzoylchloride as acylating agent using the above catalysts. (document is a template. For questions on paper guidelines, please contact us via e-mail.)

II. EXPERIMENTAL

1) *Preparation of K-10 MAA-120and K-10 MAA-550 Catalysts:* Anhydrous metal chloride (15g) was dissolved in deionized water (60 ml) and Montmorillonite K-10 clay (10g) was added over a period of 10 minutes. In case of $SbCl_3$, $BiCl_3$ and $ZrOCl_2$ conc. HCl 10 ml were used to get a clear solution of the metal chlorides. The resulting slurry was stirred at room temperature for 5 h. The clay was filtered using sintered glass Funnel (G-2), washed with deionized water to remove Cl^- ions. The paste obtained after filtration was dried in an electric oven for 2 h at 80 ˚C. The clay obtained was crushed carefully to obtain a free flowing powder, and was stored in an air tight bottle in a vacuum desiccator[18].

a) *Heat Treatment:* These catalysts were then activated at 120 ˚C and 550 ˚C separately to get K-10-MAA-120 and K-10-MAA-550 catalysts respectively. These catalysts were preserved in a vacuum desiccator and used after activation at 120 ˚C overnight[18].

2) *Preparation of K-10 MOO-120 and K-10 MOO-550 Catalysts:* Anhydrous metal chloride (15g) was dissolved in dry Acetonitrile solvent (60 ml) and Montmorillonite K-10 clay (10 g) was added over a period of 10 minutes. The resulting slurry was stirred at room temperature for 5 h. The clay was filtered using sintered glass Funnel (G-2), washed with dry Acetonitrile solvent (10 ml) and three portions of dry benzene (20 ml). The clay obtained after filtration was dried in an electric oven for 2 h at 80 ˚C. Finally, the clay obtained as a free flowing powder, was stored in an air tight bottle in a vacuum desiccator[18].

a) *Heat treatment:* These catalysts were then activated at 120 ˚C and 550 $^{\circ}$C separately to get K-10-MOO-120 and K-10-MOO-550 catalysts respectively. These catalysts were preserved in a vacuum desiccator and used after activation at 120 $^{\circ}$C overnight[18].

3) *Preparation of 4-Chloro,4'-Hydroxy Benzophenone:* In a four necked round bottom flask fitted with mechanical stirrer, addition funnel, water condenser and thermopocket, the modified K-10 clay catalyst were added and mixed with phenol in solvent. The temperature was maintained below 10˚C by keeping the reaction flask in ice bath. A solution of acetylating agent was then added from the addition funnel slowly maintaining the temperature between 25 – 30 $^{\circ}$C. After addition was completed (10-15 min) the flask from the ice bath was removed and kept on the heating mantle maintained at desired temperature with constant stirring for 5 h. The progress of the reaction was monitored by TLC qualitatively and by HPLC quantitatively. Then the flask was cooled to room temperature and filtered through G-2 sintered bed glass crucible to separate the catalyst from the reaction mixture. The catalyst was then washed 3-4 times with solvent and the filtrate and the washings were combined and the solvent was distilled out. The residue obtained was then dissolved in excess of 10% NaOH solution and filtered. The filtrate was acidified with concentrated HCl to pH 5 to get the pure product which was further purified by column chromatography using mobile phase benzene : ethyl acetate (80:20). The fraction of the eluent giving the single spot was collected and evaporated to dryness and recrystallized with methanol. The melting point of this product was carried out and characterized by IR, PMR and Mass Spectroscopy.

a) Scheme

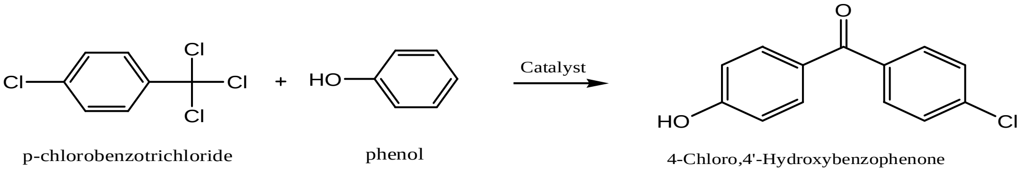


Fig. 1

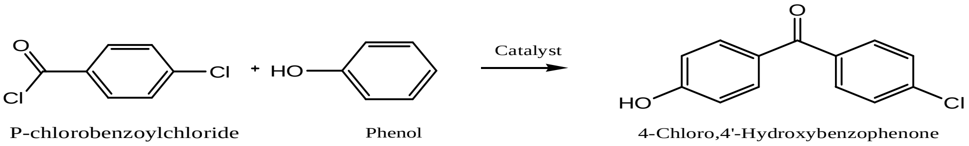


Fig. 2

III.RESULTS AND DISCUSSION

In the preparation of K10-MAA catalysts, the metal chloride was dissolved in deionized water, equilibrated for the 5h, filtered and washed with deionized water till complete removal of the chloride ions. In the preparation of K10-MOO catalysts, the metal chloride was dissolved in dry organic solvents, equilibrated for the 5h time, filtered and washed with dry organic solvents. Table I shows the various catalysts preoared.

The uptake of various Metal Chlorides by K-10 clay from aqueous and acetonitrile solutions was determined by back-titrating the supernatant solution with EDTA using appropriate indicators as described in Vogel's Textbook of quantitative chemical analysis.[19] And Zr was determined by gravimetric analysis as per procedure given in Vogel's Textbook of quantitative chemical analysis[19]. The results of the elemental analysis are as shown in table II.

Table I

Various catalysts prepared under present investigation

Metal Chloride	Solvent used for treatment	Solvent used for washing	Temperature of heat treatment ˚C	Final Catalyst
$AlCl_3$	Water	Water	120	K10-AlAA-120
			550	K10-AlAA-550
	Nitrobenzene	Nitrobenzene + Benzene	120	K10-AlOO-120
			550	K10-AlOO-550
$FeCl_3$	Water	Water	120	K10-FeAA-120
			550	K10-FeAA-550
	Acetonitrile	Acetonotrile + Benzene	120	K10-FeOO-120
			550	K10-FeOO-550
$SbCl_3$	Water + Conc HCl	Water	120	K10-SbAA-120
			550	K10-SbAA-550
	Acetonitrile	Acetonotrile + Benzene	120	K10-SbOO-120
			550	K10-SbOO-550
$ZnCl_2$	Water	Water	120	K10-ZnAA-120
			550	K10-ZnAA-550
	Acetonitrile	Acetonotrile + Benzene	120	K10-ZnOO-120
			550	K10-ZnOO-550
$ZrOCl_2$	Water + Conc HCl	Water	120	K10-ZrAA-120
			550	K10-ZrAA-550
	Acetonitrile	Acetonotrile + Benzene	120	K10-ZrOO-120
			550	K10-ZrOO-550
$BiCl_3$	Water + Conc HCl	Water	120	K10-BiAA-120
			550	K10-BiAA-550
	Acetonotrile	Acetonotrile + Benzene	120	K10-BiOO-120
			550	K10-BiOO-550

Table II
Elemental Analysis of catalyst

Catalyst	Element	Percentage
K10-FeOO-120	Fe	2.6
K10-AlOO-120	Al	2.9
K10-ZnOO-120	Zn	5.4
K10-SbOO-120	Sb	1.8
K10-BiOO-120	Bi	2.1
K10-ZrOO-120	Zr	1.6
K10-FeAA-120	Fe	2.9
K10-AlAA-120	Al	3.1
K10-ZnAA-120	Zn	4.6
K10-SbAA-120	Sb	1.9
K10-BiAA-120	Bi	1.8
K10-ZrAA-120	Zr	1.9

Yield of 4-Chloro-4′-Hydroxybenzophenone was optimized when the reaction is carried out using phenol and p-chlorobenzoylchloride with K10-Fe-AA-120 as catalysts at 40˚C (Table III). In order to investigate the effect of amount of catalyst on the reaction product, a series of reaction were carried out by various amounts of K10-Fe-AA-120 catalyst. Yield of 4-Chloro,4’-Hydroxybenzophenone increased with increasing amount of the catalyst used but the best yield was achieved when the amount of the catalyst was 1.0 g / 0.05 mole of phenol (Table IV). And further rise in the amount of catalyst did not lead to any further rise in the yield of the product.

In order to investigate the effect of various solvents and reaction temperature keeping the amounts of phenol, p-chlorobenzotrichloride / p-chlorobenzoyl chloride, catalyst and reaction time constant (Table V).

Ethylene dichloride was found to be the best solvent for the reaction. And reaction went smoothly at 40˚C to yield the product in good amount (Table V). These conditions were used for further study. The effect of reflux time required for completion of the reaction to produce 4-Chloro,4’-Hydroxybenzophenone was investigated and the results obtained are as summarized Table VI.

Reactants were mixed along with the catalyst at 30˚C. The temperature of the mixture was raised to 40˚C and the mixture was stirred continuously. The reaction was stopped after intervals of 1hr, 2h, 3h, 4h, 5h, 6h and 7h and samples were taken and analyzed by HPLC to find the percentage yield of 4-Chloro,4’-Hydroxy Benzophenone (Table VI). The percentage yield of the product was found to increase as the time of refluxing the reaction mixture from 1 to 5 h. After 5h there was no increase in the percentage yield of the product was found. Therefore, the reaction mixture was refluxed for 5 h in all other experiments.

The acylation was carried out by varying the amounts of phenol from 0.05 to 0.15 moles keeping other parameters constant.

The Results (Table VII) show that there is no effect of increase in the quantity of phenol on the product yield. The acylation was carried out by varying the amounts of p-chlorobenzotrichloride and keeping the other parameters constant.

When the amount of p-chlorobenzotrichloride was increased in the reaction the percentage yield of the product did not increase (Table VIII). The acylation was carried out by varying the amounts of p-chlorobenzoylchloride and keeping the other parameters constant (Table IX).

It was found that there is no significant effect on product yield by varying the amount of p-chlorobenzoylchloride (Table IX).

Therefore, it is evident from all the above reactions that the maximum yield of the product is obtained by the reaction of Phenol and p-chlorobenzoylchloride using K10-FeAA120 catalyst in ethylene dichloride as a solvent at 40˚C. This is also confirmed testing the Melting point of the compound which is found to be 175-177˚C. IR, NMR and Mass spectra of the product obtained is found to be super imposing the standard compound.

Table III

Percentage Yield of reaction product at 40˚C and 80˚C.

Catalysts	% yield of 4-chloro,4'-hydroxy benzophenone at 40˚C		% yield of 4-chloro,4'-hydroxy benzophenone at 80˚C	
	PCBTC + Phenol	PCBC + Phenol	PCBTC + Phenol	PCBC + Phenol
K10-Al-AA-120	62.5	64.6	67.8	68.2
K10-Al-AA-550	60.5	60.9	63.9	65.7
K10-Al-OO-120	61.5	65.3	67.8	64.2
K10-Al-OO-550	58.2	57.8	66.1	65.3
K10-Sb-AA-120	65.3	67.8	66.4	66.5
K10-Sb-AA-550	64.5	66.5	62.1	64.7
K10-Sb-OO-120	66.4	68.9	70.6	70.1
K10-Sb-OO-550	62.1	66.8	64.5	69.8
K10-Fe-AA-120	69.2	96.7	73.8	95.1
K10-Fe-AA-550	61.5	96.5	70.1	91.4
K10-Fe-OO-120	73.5	87.4	73.6	91.7
K10-Fe-OO-550	86.8	93.5	80.8	87.5
K10-Zn-AA-120	72.2	73.1	70.5	70.1
K10-Zn-AA-550	69.4	69.6	68.9	69.1
K10-Zn-OO-120	74.1	71.9	75.3	71.7
K10-Zn-OO-550	73.6	73.2	71.4	70.5
K10-Zr-AA-120	61.5	60.3	67.7	64.4
K10-Zr-AA-550	59.8	60.9	62.7	62.3
K10-Zr-OO-120	62.1	63.8	62.4	62.3
K10-Zr-OO-550	56.4	60.1	61.3	61.7
K10-Bi-AA-120	64.1	63.3	62.9	63.8
K10-Bi-AA-550	61.2	61.1	60.6	60.2
K10-Bi-OO-120	65.2	65.4	63.3	62.7
K10-Bi-OO-550	58.5	60.2	61.1	61.5

Phenol-0.05 mole; p-chlorobenzotrichloride / p-chlorobenzoyl chloride - 0.05 mole ; (Solvent) Ethylene dichloride-100ml; Temperature- 40˚C & 80˚C; Time- 5h

Table IV

Effect of amount of catalyst.

		% Yield of 4-Chloro,4'-Hydroxy Benzophenone (by HPLC)							
Catalyst		K10-Fe-AA-120		K10-Fe-AA-550		K10-Fe-OO-120		K10-FeOO550	
Reactants									
Sr. no.	Amt of Catalyst (in g)	PCBTC	PCBC	PCBTC	PCBC	PCBTC	PCBC	PCBTC	PCBC
1	0.1	4.1	5.1	No reaction	2.7	3.4	4.7	3.9	5.7
2	0.5	30.3	34.6	23.3	26.6	29.4	38.6	33.5	36.2
3	1.0	69.2	96.7	61.5	96.5	73.5	87.3	86.8	93.5
4	2.0	69.2	96.7	61.3	96.4	73.4	87.4	86.8	93.4
5	3.0	69.2	96.7	61.3	96.6	73.5	87.4	86.6	93.4

Phenol-0.05 mole; p-chlorobenzotrichloride / p-chlorobenzoyl chloride - 0.05 mole ; (Solvent) Ethylene dichloride-100ml; temperature- 40˚C; time- 5h.

Table V
Effect of various solvents and reaction temperature.

Sr. No.	Solvent	Reaction Temperature	% Yield of 4-Chloro,4’-Hydroxy Benzophenone (by HPLC)	
			PCBTC	PCBC
1	Methylene Dichloride	20˚C	Did not react	Did not react
		30˚C	15.2	16.5
		40˚C	28.1	40.3
2	Ethylene Dichloride	20˚C	8.5	10.9
		40˚C	70.5	96.7
		60˚C	71.2	96.2
		80˚C	73.8	95.1
3	Ethyl Acetate	20˚C	Did not react	5.1
		40˚C	Did not react	10.8
		60˚C	4.2	12.3
		80˚C	4.5	20.1
4	Chloroform	20˚C	Did not react	20.3
		40˚C	Did not react	25.1
		60˚C	16.6	39.8
		80˚C	16.9	42.7
5	Chlorobenzene	20˚C	Did not react	3.8
		40˚C	3.4	5.6
		60˚C	8.8	10.5
		80˚C	21.9	25.3

Phenol-0.05 mole; p-chlorobenzotrichloride / p-chlorobenzoyl chloride - 0.05 mole; K10-FeAA120-1g; Time- 5h.

Table VI
Effect of time of reflux.

Sr. No.	Time in H	% Yield of 4-Chloro,4’-Hydroxy Benzophenone (by HPLC)	
		PCBTC	PCBC
1	1	70.6	78.1
2	2	70.9	92.9
3	3	69.9	95.1
4	4	70.5	96.2
5	5	70.5	96.7
6	6	70.5	96.7
7	7	70.5	96.7

Phenol- 0.05 mole, p-chlorobenzotrichloride / p-chlorobenzoyl chloride – 0.05 mole, Solvent EDC – 100 ml, K10-FeAA120 – 1g, Temperature – 40˚C.

Table VII
Effect of variation of Phenol.

Sr. No.	Amount of Phenol	% Yield of 4-Chloro,4'-Hydroxy Benzophenone (by HPLC)	
		PCBTC	PCBC
1	4.7	70.5	96.7
2	7.05	70.5	96.7
3	9.4	70.9	96.7
4	14.1	71.1	97.8

p-chlorobenzotrichloride / p-chlorobenzoyl chloride – 0.05 mole, Solvent EDC – 100 ml, K10-FeAA120 – 1g, Temperature – 40˚C, Time – 5 h.

Table VIII
Effect of variation of p-chlorobenzotrichloride.

Sr. No.	Amount of p-chlorobenzotrichloride	% Yield of 4-Chloro,4'-Hydroxy Benzophenone (by HPLC)
1	11.5	70.5
2	17.2	70.6
3	23	70.6

Phenol – 0.05 mole, Solvent EDC – 100 ml, K10-FeAA120 – 1g, Temperature – 40˚C, Time – 5 h.

Table IX
Effect of variation of p-chlorobenzoylchloride.

Sr. No.	Amount of p-chlorobenzoylchloride	Yield of 4-Chloro,4'-Hydroxy Benzophenone (by HPLC)
1	8.8	96.7
2	13.2	96.7
3	17.5	96.7

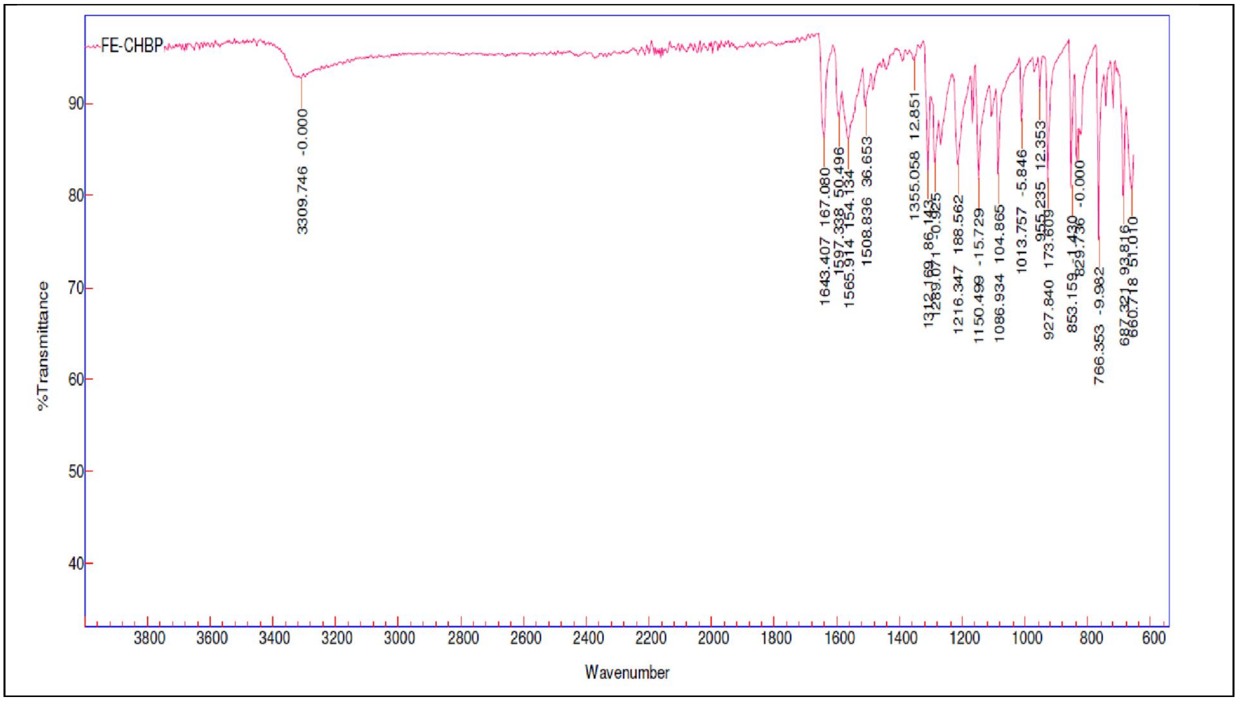
Phenol – 0.05 mole, Solvent EDC – 100 ml, K10-FeAA120 – 1g, Temperature – 40˚C, Time – 5 h.

IV.CONCLUSION

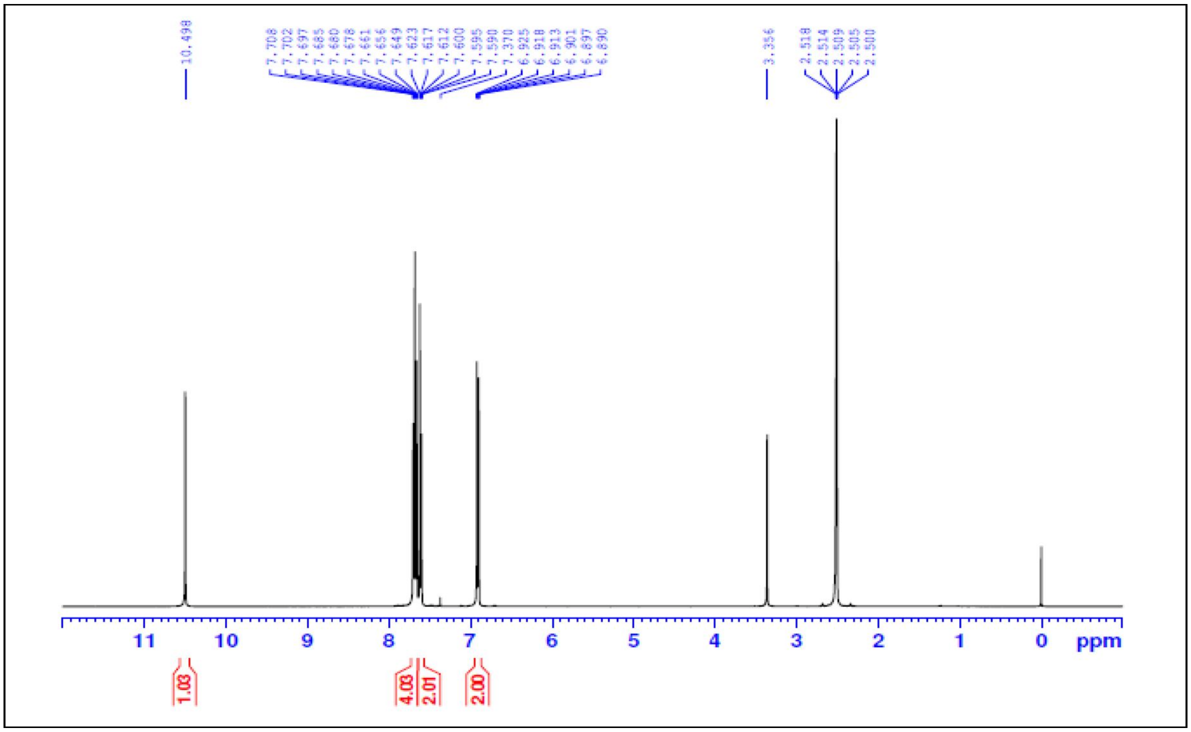
In conclusion, out of the various heterogeneous catalysts used K10-FeAA120 catalyst works best for the conversion at 40˚C using ethylene dichloride as solvent. Easy separation of the heterogeneous catalyst makes the protocol eco-friendly and efficient than conventional methodologies. The optimized procedure is efficient if used at an industrial scale. In future scope we propose that the catalyst recovered can be regenerated and reused.

V. SUPPLEMENTRY DOCUMENTS

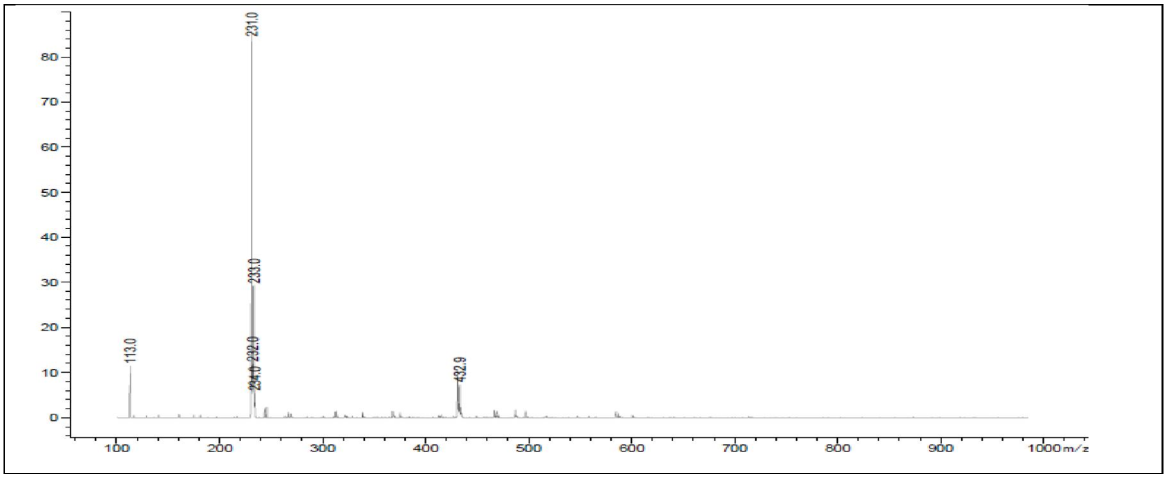
Infrared Spectrum of 4-Chloro,4’-HydroxyBenzophenone



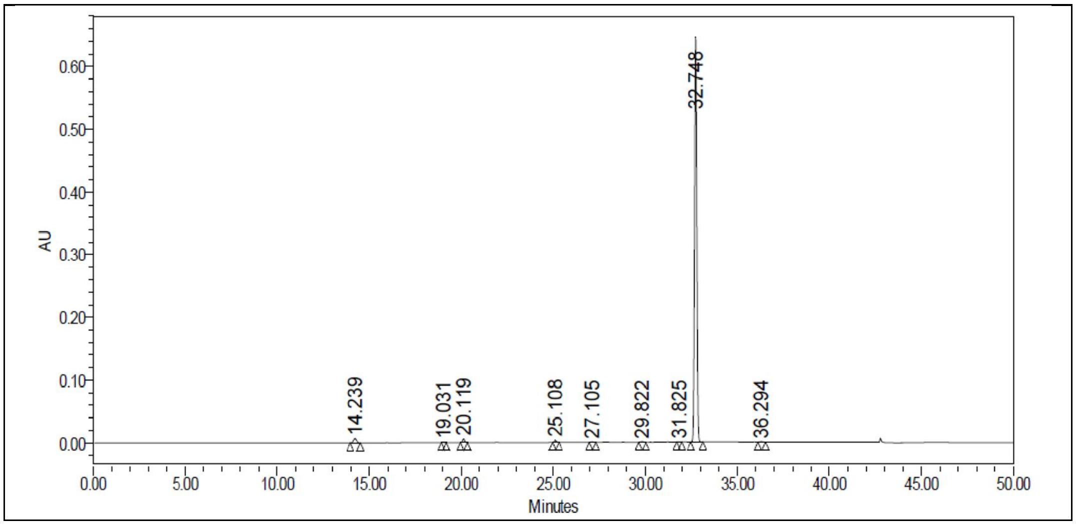
Nuclear Magnetic Resonance Spectroscopy of 4-Chloro,4’-HydroxyBenzophenone



Mass Spectrum of 4-Chloro,4'-HydroxyBenzophenone



PLC report of Reaction Mass of reaction between Phenol and P-chlorobenzoyl chloride at 40°C.



	RT	Area	% Area
1	14.239	78466	1.43
2	19.031	3134	0.06
3	20.119	46899	0.85
4	25.108	24459	0.44
5	27.105	8680	0.16
6	29.822	8893	0.16
7	31.825	3084	0.06
8	32.748	5316875	96.71
9	36.294	7354	0.13
None			

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