Benzylation of chlorobenzene over M-Ferrites $M^{2+}Fe^{3+}O_4(M^{2+}= Fe^{2+}Zn^{2+}, Ni^{2+}, Cd^{2+}, V^{2+})$

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Abstract:

A series of $M^{2+}Fe^{3+}O_4(M^{2+}$represent $Fe^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, V^{2+})$ ferrites were synthesized by co-precipitation of M-Ferrites normally soluble under controlled conditions. The synthesized ferrites were used as a catalyst to benzylatechlorobenzene usingbenzylchloride. The effects of some parameters, such as temperature, a molar ratio,type;amount, reusabilitytest and leaching test of catalyst were followed. The optimum conditions appliedwere (80ºC, ١:15 for benzylchloride/chlorobenzene, 0.1g as weight of catalyst and Fe-Fer.as type of catalyst). The reaction products were invistigatedusing GC chromatograph equipped with FID detector. The results showed that when M-ferrites were used for benzylation ofchlorobenzene,very high efficient catalytic activityabout 90% for the conversion ofchlorobenzene tochlorodiphenyl methane (CDPM) was obtained. The synthesized M-Ferrites were successfully used as heterogeneous and magnetically recoverable catalyststo benzylationreaction. Thebenzylation reaction was observedas not toproceed in the absence of M- ferrite catalysts.

Key words:Benzylation,chlorobenzene, ferrite, heterogeneous, leaching.

مستخلص:

تم تحضير سلسلة من حفازات الحديدبطريقة الترسيب المتزامن. ثم استخدام حفازات الحديد المحضرة أعلاه كعامل حفازلبنزلهالكلوروبنزين باستخدام كلوريد البنزين . تم دراسه تأثير بعض العوامل مثل درجه الحراره , النسبه المولیه , نوع الحفاز, الكميه وأعادة الاستخداماللعامل الحفاز . ووجد أن الظروف المثلي للتفاعل هي درجه الحراره 80 درجه مئويه , النسبه المولیه 1:15 ,وزن الحفاز 0.1 جم ,ونوع الحفاز( ). تمت متابعه التفاعل باستخدام جهاز كروتوغرافيا الغاز المجهز بكاشف التأين باللهب . أظهرت النتائج ان حفازات الحديد تمتلك فعاليه عاليه 90 % في تنشيط تفاعل بنزله الكلورو بنزين. ونجح العامل الحفاز في اعادة استخدامه مرة اخري كحفاز غير متجانس لتفاعل البنزله . لوحظ أن التفاعل لايحدث في حاله عدم وجود الحفاز .

كلمات مفتاحية: بنزله , الكلورو بنزين ,حفازات الحديد الغير متجانس, ترشيح .

1. Introduction:

Recent Studies to develop new types of catalytic compounds to replace liquid acids with solid acid catalysts to enhance catalytic activity, to minimize hazard products were cited[1]. Among the important catalysts used in the last 50 years, are the ferrite compounds. Ferrites work as catalysts in benzylation reactions (1). Liquid–phase benzylation of aromatic compounds using benzyl halides or alcoholsis a very important reaction in many industrial processes such as the synthesis of pharmaceuticals, dyes, fragrance and agrochemicals[2].Benzylation reaction is a process by benzene and benzene derivatives like toluene, chlorobenzene and xyleneby which react with benzyl halides to produce diphenylmethane(2).Friedel–Crafts alkylation reaction is a typical electrophilic aromatic substitution and involves initially the formation of complex intermediates, i.e. “σ-orπ-complexes” between the alkyl halide and the metal halide catalyst[3]. This reaction is also considered to be a nucleophilic substitution reaction, because it involves a nucleophilic attack by aromatic ring on the alkyl group(3). The first typical Friedel-Crafts alkylation reaction was the reaction of benzene (aromatic) with amyl chloride (alkylating agent) in the presence of $AlCl_3$to produce amyl benzene(4).

The effects of some parameters, such as temperature, types of catalyst, molar ratio of reactants were investigated(5). Synthesis series of ferrite oxides compounds, ferrite-iron, ferrite-nickel, ferrite-zinc, ferrite-cadmium and ferrite vanadium. Ferrites were synthesized according to M-Fe_2O_4formula (M represent Fe^{+2}, Zn^{+2},Ni^{+2}, Cd^{+2}, V^{+2}) under optimized conditions. The synthesized ferrites were characterized by powder X-ray diffraction pattern(X-RD),Atomic Absorption Spectrometry(AAS), Ultraviolet Spectrometry (UV), Inductively coupled plasma – optical emission spectrometry (ICP-OES) and Gas Chromatography (GC) was used to follow thebenzylation reaction and to detect the highest conversion percentage. Ferrites are a large class of oxides with remarkable magnetic properties, which have been investigated and applied during the last ~50 years(6). Ferrites or ferromagnetic oxides (also known as ceramics containing compounds of iron) are dark brown or gray in appearance and very hard and brittle in texture(7) . Their application encompass wide range extending from millimeter wave integrated circuitry to power handling, simple permanent magnets , and magnetic recording(8).

The main objectives of this study their catalytic activity, the ferrites were prepared as heterogeneous catalysts, for theFriedel-Craftsbenzaylation reaction of chlorobenzene with benzyl chloride.

2.**Materialsand Methods**

2.1 Chemicals

Ferrous sulphatehepta-hydrate, $FeSO_4.7H_2O$, (Min. assay 98%, Prabhat chemicals).

- Barium (II) chloride, $BaCl_2$, (Min. assay 96%, Prabhat chemicals).
- Hydrochloric acid HCl, (Density 1.18 g/Cm3, Min. assay 35-38%, Lobachemie .Pvt Ltd, India).
- Sulphuric acid solution, H_2SO_4, 10%.
- Distilled water
- Sodium Hydroxide pelletsNaOH (Min assay: 98%, LOBA Chemie, India)
- Sodium Nitrate, $NaNO_3$(Min. assay 87%, Scott science, UK).

- Ammonium oxalate monohydrate, $(NH_4)_2C_2O_4.H_2O$, Min. assay 97%, Prabhat Chemicals).
- Zinc Sulphate, $ZnSO_4$.(Min.assay 95 % ,prabhat chemicals).
- Nickel Nitrate, Ni NO_3.(Min. assay 87%, Scott science, UK).
- Cadmium Sulphate, $CdSO_4$. (Min.assay 95 %, prabhat chemicals
- Ammonium Meta vanadate, CDH, China.
- Paraffin oil (SIGMA –ALDRICH).
- Acetone (Panera, 99.5 %).

All chemicals are of Analytic Grad typied.

2.2Apparatus and Instruments

- Sensitive balance, A.A220.B, RAWAG WAGI Elektroniczne, Poland (EU).
- Hotplate/stirring, Dlab Tech, DAIHANLABTECH CO., LTD, Kore
- Muffle furnace.
- Atomic Absorption Spectrometry Sauant AA, GBC scientific equipment Pty Ltd, GBC, A 7804, Australia.
- X-RAY Diffraction (XRD) (Panan analytical X Pert3 MRD), Netherland. Rate of 10°C/min.
- Ultra violet Spectrometry UV/VISIBLE -Model 7205, JENWAY, UK.
- Inductively coupled plasma – Optical Emission Spectrometry (ICP- OES) Plasma Quant –PQ9000, Analytic Jana, and Germany.
- Gas chromatograph, GC 2010, Column type: capillary column BD-210, Column: Low polarity phase.

2.3 Methods

2.3.1 Synthesis of ferrites

(i)Synthesis of Magnetite, Fe_3O_4 “Fe^{II} [$Fe_2^{III}O_4$]”

9.265 g of $FeSO_4.7H_2O$ was dissolved in 307.8 cm^3 of distilled water. 0.2827 g of $NaNO_3$ and 5.0269 g NaOH were dissolved in 33 cm^3 distilled water. Each solutions were heated to about 75°C, then mixed together by vigorous stirring. A thick gelatinous green precipitate was formed. After that stirred at 90°C to 100°C for 10 min, the precipitate was turned to a finely divided dense black substance. The mixture was cooled at room temperature and it acidic with a little 6M HCl. Filtered the precipitate and washed with distilled water until the wash water given no test for sulfate with $BaCl_2$ solution. Dried the material at 110 °C for 2 hours then weighed it. [9]

$$12Fe^{2+} + 23OH^{-} + NO^{3-}4Fe_3O_4 + NH_3 + 10H_2O$$

(ii) **Synthesis of M^{2+} Ferrite ($M^{2+}Fe_2O_4$)**

A mixture of M^{2+} $FeSO_4.7H_2O$ and 10% H_2SO_4 were dissolved in distilled water. While $(NH_4)_2C_2O_4.H_2O$ dissolved in warm distilled water. The solution heated to about 75°C with stirring vigorously,addoxatate solution to the metal sulfate solution . The mixture Stirred tell the temperature rich from 90°C to 95°C for about 5 min. The yellow mixed oxalate precipitate was filtered on a sintered–glass funnel and wash with distilled water until sulfate no longer be detected in the wash water (it used $BaCl_2$ solution for this purpose). The oxalate precipitate dried for several hours at 110°C. The mixed oxalate precipitate transferred to a50 cm-3 crucible with a cover and place the covered crucible in a muffle and heated to 600°C - 800°C for 3 hours. Allowed the material to cool to room temperature and weighed it(9) .

$$M^{2+} + 2Fe^{2+} + 3C_2O_4^{2-} \rightarrow M^{2+}Fe_2\,(C_2O_4)_3$$

$$M^{2+}Fe_2\,(C_2O_4)_3\,(\Delta) \rightarrow M^{2+}Fe_2O_4 + 2CO_2 + 4CO$$

2.3.2 Characterizionof ferrites

Synthesized ferrites were characterized by; X-ray diffraction pattern (XRD), atomic absorption spectrometry (AAS) and Ultraviolet spectrometry (UV).

All results confirm that the ferrites are formed.

2.3.3 Catalytic Benzylation reactions

All Catalytic benzylation reactionswere carried out in a magnetically stirred two necked round-bottomed flask (50 cm^3) fitted with a reflux condenser. The temperature of the reaction vessel was maintained precisely at the studied temperatures using an oil bath at (70ºC,80ºC,90ºC, 100ºC).The reactions were conducted under atmospheric pressure. In typical chlorobenzene (CB) reaction 1.0 cm^{3} of n-octane (internal standard for benzylationreactions) and 23.0 cm^{3} ofchlorobenzene(CB) were added 0.1 g of the catalyst (which had been activated temperature.This was followed by 2.0 cm^{3} of benzyl chloride(BC) to obtain the required CB/BC molar ratio of 15:1. Ratios of 10:1, 20:1 and 5:1 were also studied for benzylation reactions at optimum temperature. The benzylation reaction of chlorobenzene was conducted by taking reactant quantities equivalent to the prescribed molar ratios following the previous procedure. The total volume of the reactants was kept at 25.0 cm^{3}for all the catalytic reactions.However, to monitor the progress of the reaction,aliquot of the hot mixture (0.5 cm^{3}) were withdraw at regular intervals utilizing a syringe.The clear solution was analyzed by GC using appropriate conditions as presented in Table 1:1.

Table 1.1: The GC conditions for the separation and identification of the benzylation reactionproduct.

Conditions	Benzylation ((BC	Benzylation (Aromatics)	Products (BC +Aromatics)
Initial temperature	90ºC	ºC 90	ºC 40
Initial time	min 0	min 0	min 2
Ram	min 10	min 10	min 20
Final temperature	220ºC	ºC 220	ºC 220
Final time	min 3	min 5	min 5
Injector temperature	ºC 250	ºC 250	ºC 250
Detectortemperature	ºC 250	ºC 250	ºC 250
Carrier gas	Nitrogen	Nitrogen	Nitrogen
Flow rate	3ml min^{-1}	3ml min^{-1}	3ml min^{-1}

A reusability experiment was conducted by running the reaction successively with the samecatalyst under the same reaction condition without any regeneration between three runsaccording to the reported method (10,11). The reaction was first run with the fresh catalyst to completeconversion, and then the supernatant liquid reaction mixture was sucked out carefully employing a syringe avoiding the removal of the catalyst[12]. Fresh reactants were introduced following thesame sequence and composition(13). The products were analyzed by GC using the conditionspresented in Table 1.1.

A leaching experiment was carried out typified by filtering and activating the catalyst. The solidwas quickly returned to a clean flask maintained at the same reaction temperature and thereaction was allowed to proceed further(14).

3. Results and discussion

3.1 Yields of synthesized ferrites

Four types offerrites were prepared from hydrated Iron (II) sulfate and salt of(Fe^{2+} , Zn^{2+} , Ni^{2+}, Cd^{2+} and V^{2+}).These ferrites include Iron ferrite (Fe-Fer.), Zinc ferrite (Zn-Fer.), Nickel ferrite (Ni-Fer.),Cadmium(Cd-Fer) and Vanadium ferrite (V-Fer.).The appearances and yields percentage ofthe produced ferrites are illustrated in table 3.1. The colours of these ferrites are similar, withexception of Fe-Fer. and Ni-Fer. All the yields percentage of synthesized ferrites a bout > 90.

Table 1.2: The yields of as-synthesized ferrites

No	M-Ferrite	Appearance	Weight/g	%
1	(Iron ferrite(Fe-Fer	Black powder	12.58	90<
2	(Zinc ferrite (Zn-Fer	Brown powder	32.008	90<
3	(Nickel ferrite (Ni-Fer	Dark brown powder	32.385	90<
4	Cadmium ferrite ((Cd-Fer	Brown powder	33.66	90<
5	Vanadium ferrite ((V-Fer	Brown powder	27.066	90<

The conversion and selectivity calculated according to:

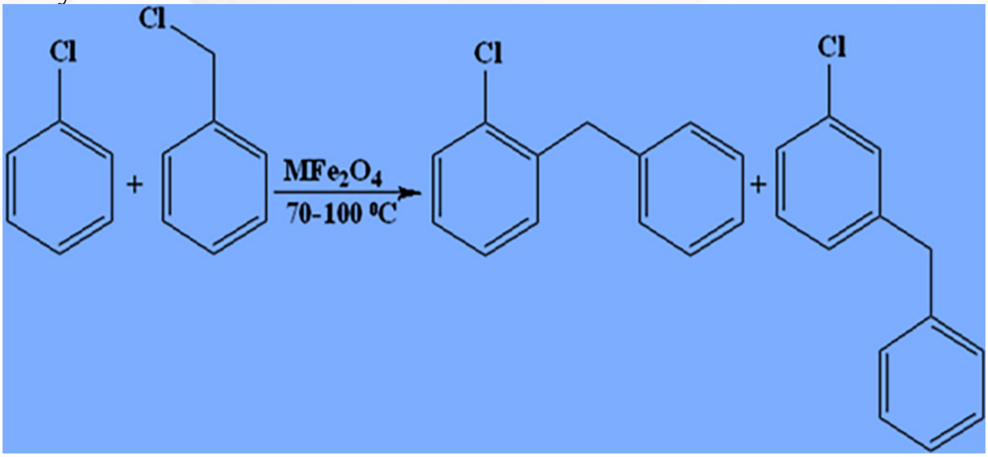
Conversion % = $(1 - A_t/A_0)$ X 100

A_t= , A_0 =(BC = Benzyl chloride, SD = Standard)

Selectivity % = (A of product /A of product +A ofStandard) X 100

3.2 Catalytic study

The liquid phase benzylation of chlorobenzene was conducted over the synthesized ferrite catalysts atdifferent conditions using benzyl chloride as benzylating agent. The reaction was schematicallylustrated in scheme 1:1.



Scheme 1.1 :Reaction scheme for the benzylation of chlorobenzene(CB) with benzyl chloride(BC) overferrite catalysts.

The products of this reaction were detected by GC chromatograph and the result isillustrated in figures[1.1 ,1.2 ,1.3,1.4] for each parameter.

3.2.1 Influence of reaction temperature

The benzylation ofchlorobenzene was carried out at different reaction temperatures using 0.1 g ofFe-Fer and BC/CB molar ratio of 1:15. The catalytic performance of the catalyst changes withtemperature. The reaction of chlorobenzene with benzyl chloride was studied at 70ºC, 80ºC, 90ºC,and 100ºC. The optimum temperature for this reaction is 80ºC as shown below inFigures. The Fe_3O_4 showed a very high catalytic proportion with increased-temperature.

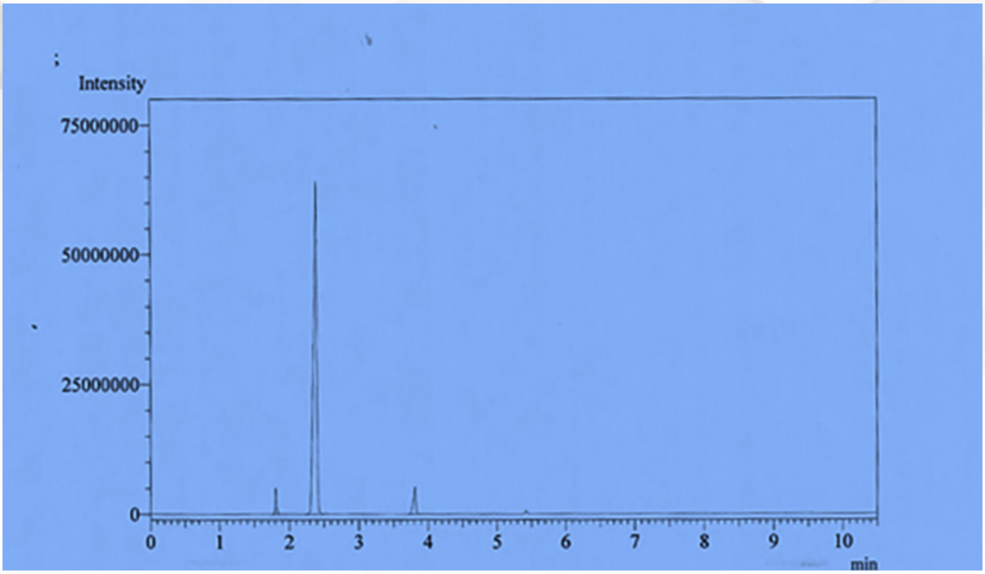


Figure 1.1 : GCchromatogram of catalytic (0.1g Fe-Fer) benzylation (BC) reaction products of chlorobenzene (CB) in the molar ratio (BC/CB) of 1: 15) at 80 ºC (0 time) .

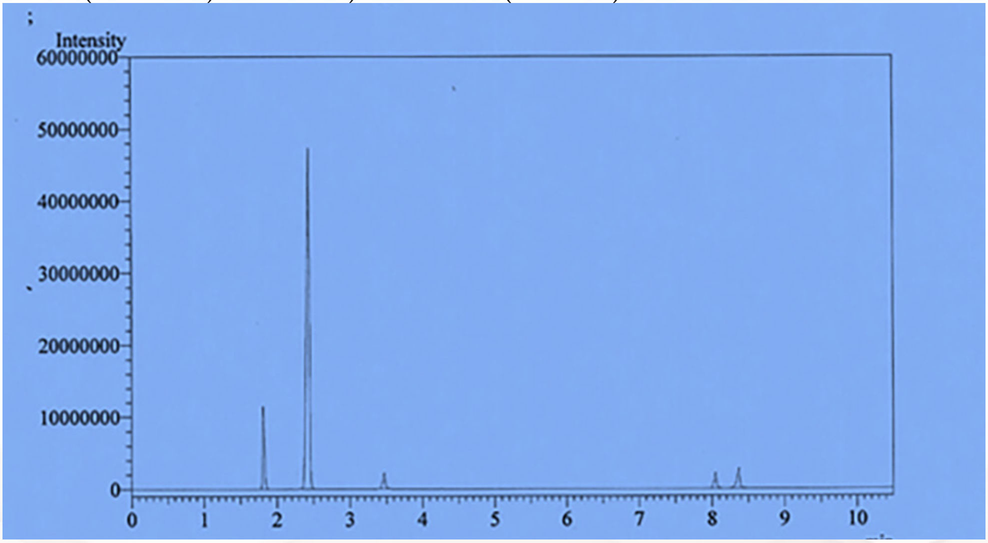


Figure 1.2 :GCchromatogram of catalytic (0.1g Fe-Fer) benzylation (BC) reaction products of chlorobenzene (CB) in the molar ratio (BC/CB) of 1: 15) at 80 ºC (5 min).

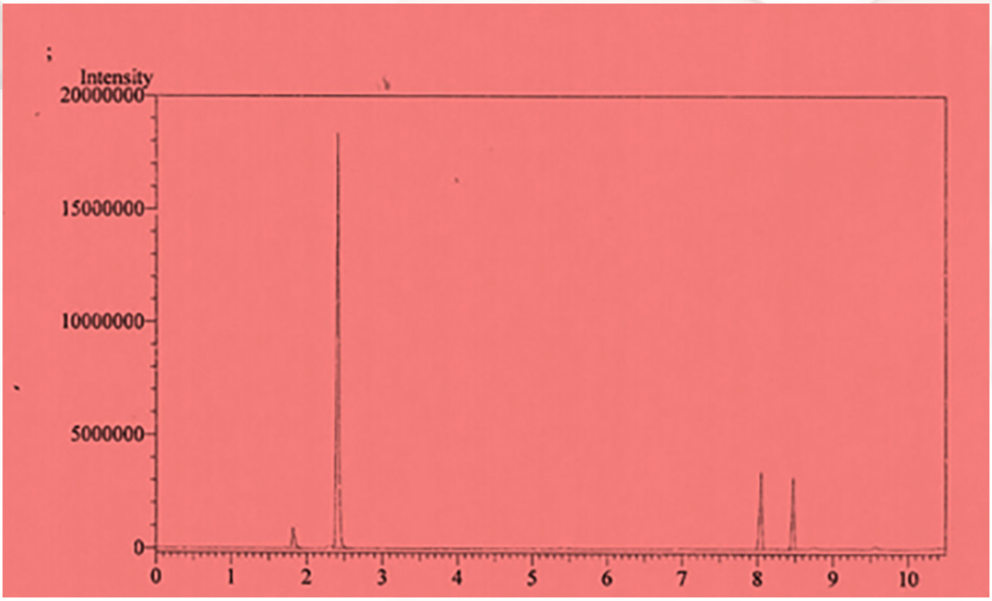


Figure 1.3 : GCchromatogram of catalytic (0.1g Fe-Fer) benzylation (BC) reaction products of chlorobenzene (CB) in the molar ratio (BC/CB) of 1: 15) at 80 ºC (complete reaction).

Table 1:3 Studyeffect of the temperature on benzylation ofchlorobenzene over Fe-Ferrite with BC atmolar ratio 1:15

Temperature / ºC	Conversion	% Selectivity	
	Time /min	B^*_1	B^*_2
70	min 10	32	66.9
80	min 5	32	67.5
90	min 2	33.2	65.3
100	min 1	32.6	65.8

3.2.2 Influence of reactants molar ratio:

The molar ratio forbenzylation ofchlorobenzene was carried out at 80ºC with various BC/CB molarratios using 0.1 g of Fe-Fer as a catalyst. The overall activity and selectivity over this catalyst werefound to increase with increasing BC: CB molar ratio as shown below

Table 1:4: Study the molar ratio effect ofbenzylation of chlorobenzene over Fe-Ferrite with BC at 80ºC

Molar ratio	Conversion Time / min	% Selectivity *B_1*	 B_2
1:5	min 1	32	63.3
1:10	min 2	32.2	63.5
1:15	min 5	34,6	64
1:20	min 10	34	63.6

3.2.3 Influence of catalyst type:

The effect of catalyst type was investigated at the optimum conditions (i.e. at 80 °C and BC: CBmolar ratio of 1:15) using either Ni- Ferrite, Zn- Ferrite, Cd- Ferrite and V- Ferrite asalternative catalysts beside Fe- Ferrite. The activity of Fe- Fer in this reaction was found to behigh, but lower than that of M-Fer, since the almost complete conversion of BC was observedwithin less than 10 minutes overall catalysts, time conversion was 100% with all it. Thepercentage selectivity is about63-64.5% forCB.

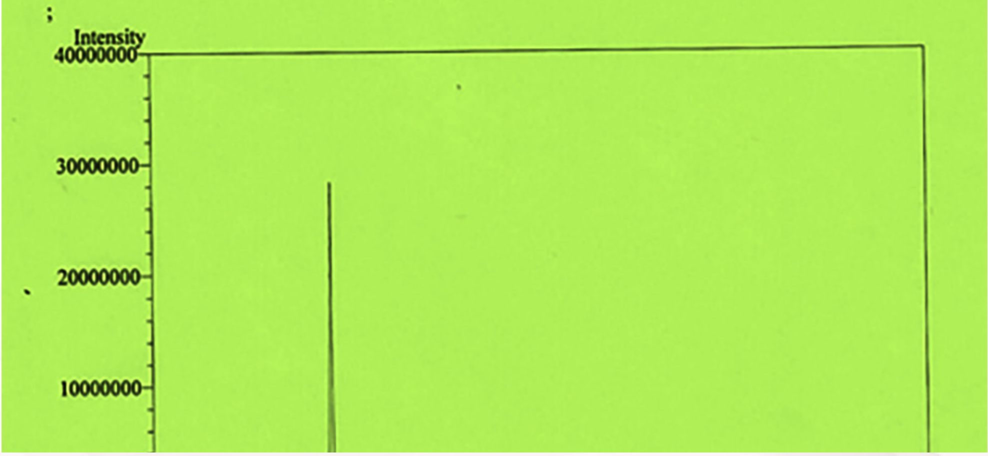


Figure 1.4: GC Chromatogram of catalytic (0.1g Zn-Fer) benzylation (BC) reaction products of chlorobenzene (CB) in the molar ratio (BC/CB) of 1: 15) at 80 ºC

Table 1:5: Study the catalyst type effect of benzylation ofchlorobenzene over Fe-Ferrite with BC at80 °C

Catalyst type	Conversion	Selectivity	
	Time / min	*B$_1$*	B$_2$
Zn-Fer	min 2	33	63.6
Ni –Fer	min 3	32.4	63.5
Cd-Fer	min 5	32	63.3
V –Fer	min 8	32.2	63.0

3.2.4 Influence weight of catalyst:

The effect of catalyst weight was studied at 80 °C for CB/BC molar ratio of 15:1 using 0.05,0.07,0.10 and 0.15 g of Fe-fer. Table 1.4showsthat the conversion of BC increases when the mass ofthe catalyst was increased, the conversion about 63-64.6% for CB.

Table 1:6: Study the catalyst weight effect of benzylation of chlorobenzene over Fe-Ferrite with BCat 80 ºC.

Catalyst wright/ g	Conversion	Selectivity	
	Time/min	*B$_1$*	B$_2$
0.05	min 4	32	65.6
0.07	3min	32.2	64.4
0.1	1min	65.634.6	
0.15	sec 40	34	64.1

3.2.5 Reusability and leaching tests

The effect of reusability of catalyst (0.1g Fe –Fer)for benzylation(BC)of chlorobenzenemolar ratio 1:15,at 80ºC,wasstudied.After the first run, 2 cm3 of benzyl chloride (BC) was added and the reaction was allowed to proceed.These steps were repeated after the second and third runs. The data shown in table(1:7) and Fig (1.5,1.6 and1 .7) result shown a decrease in catalyst activity after the catalyst re-used more than two times. The leaching experiment showed no reaction for 30 minshown in fig(1.8 and 1.9).

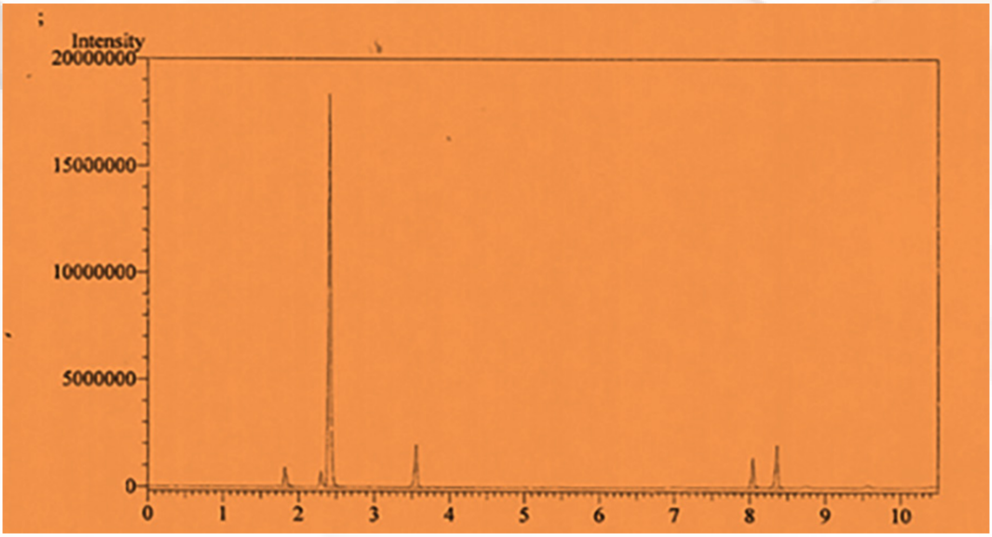


Figure 1.5: GCchromatogram of the fresh re –use of catalytic (0.1g Fe -fer) benzylation (BC) reaction products of chlorobenezene (CB) in the molar ratio (BC/CB) of 1: 15 at 80 ºC

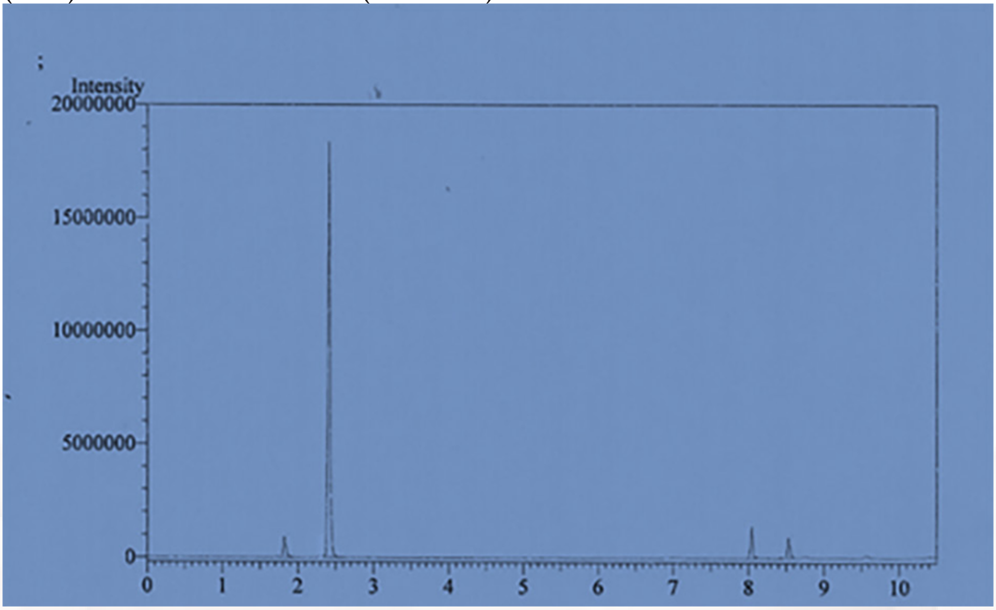


Figure1.6: GC chromatogram of the1st reuse of catalytic (0.1g Fe -fer) benzylation (BC) reaction products of chlorobenezene (CB)

in the molar ratio (BC/CB) of 1: 15 at 80 ºC

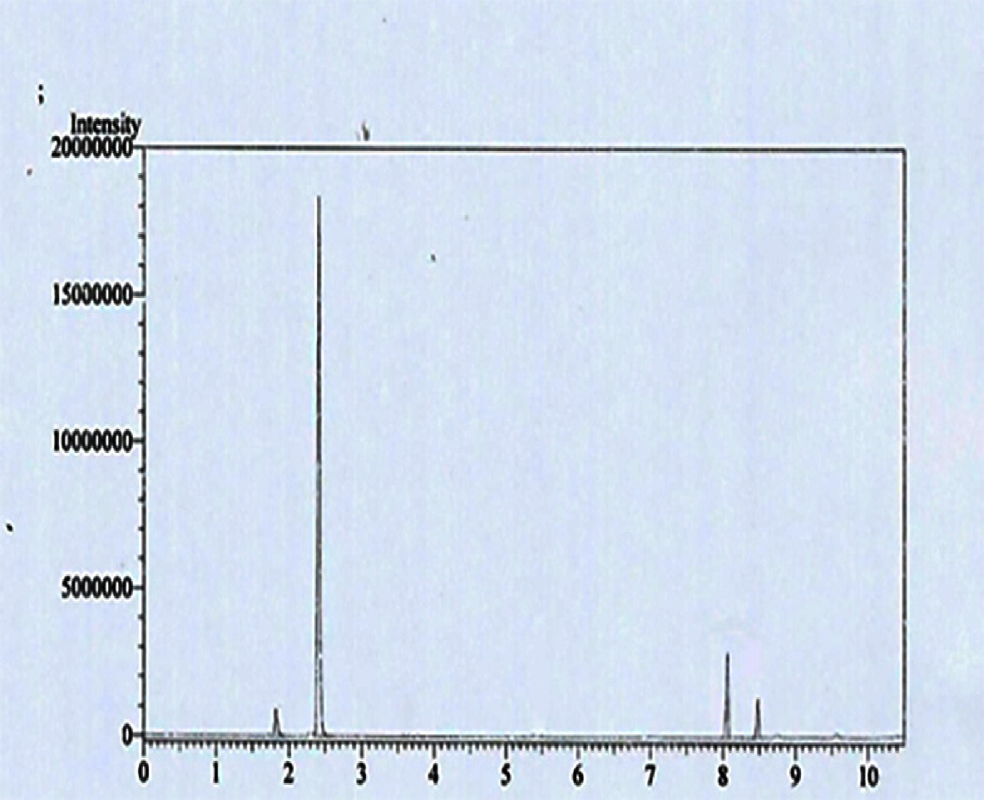


Figure1.7: GC chromatogram of the2ned reuse of catalytic (0.1g Fe -fer) benzylation (BC) reaction products of chlorobenezene (CB) in the molar ratio (BC/CB) of 1: 15 at 80 ºC

Table 1.7: Reusability of ferrites catalyst for the benzytaion of chlorobenzene at 80 ºC using CB /BC molar ratio 15:1

Recycle	**Conversion**	**Selectivity**	
	Time /min	***B$_1$***	**B$_2$**
*Fresh	sec 30	34.3	65.7
1st re-use	min 1	33.0	63.0
2st re-use	min 1.5	32.1	63.2

Fresh* time for 99.1% conversion

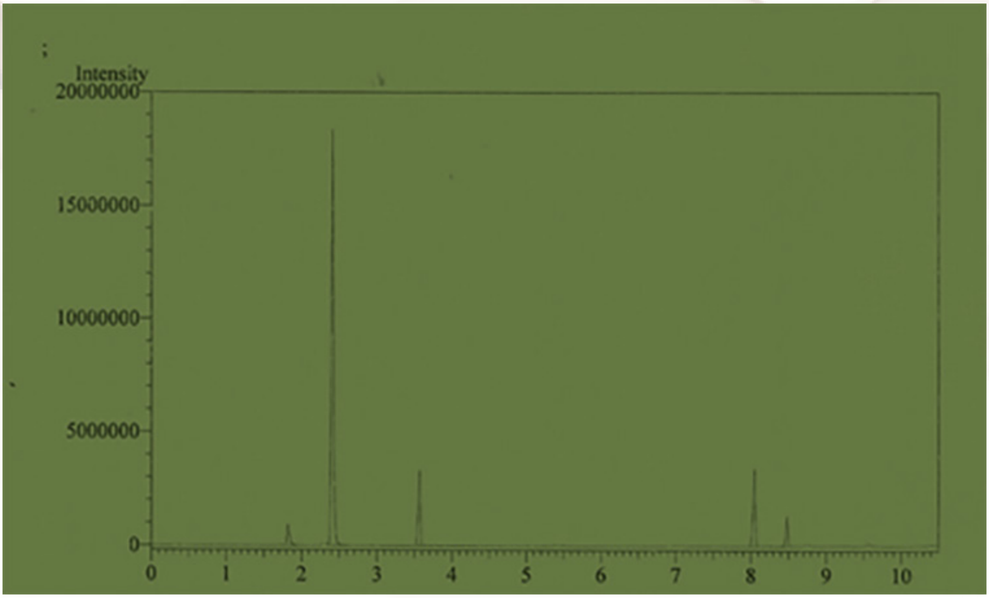


Figure 1.8: GC chromatogram of catalytic (0.1g Fe -fer) benzylation (BC) reaction products of chlorobenezene (CB) in the molar ratio (BC/CB) of 1: 15 at 80 ºC (5 mim)

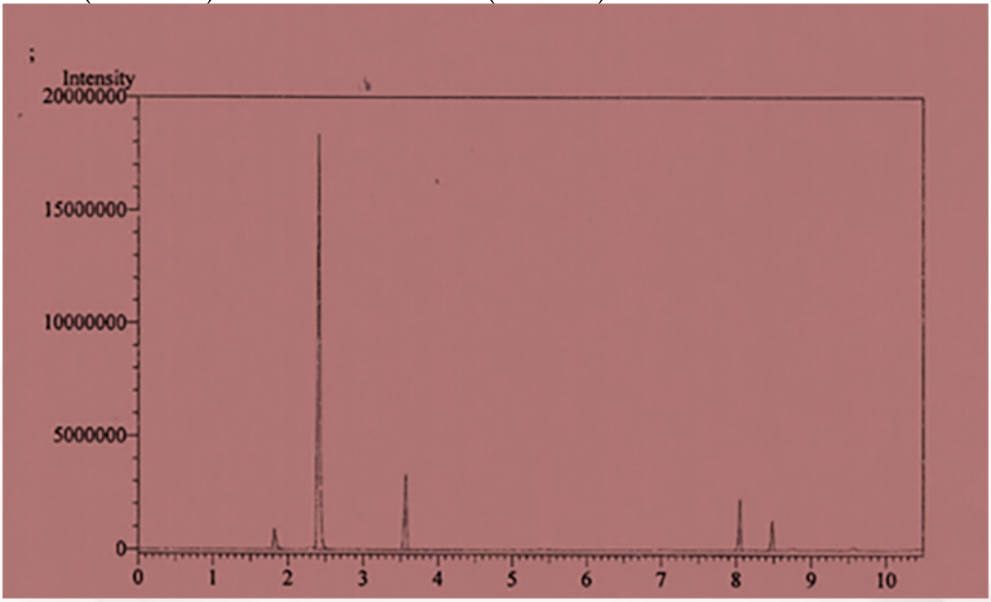


Figure 1.9: GC chromatogram of catalytic (0.1g Fe -fer) benzylation for (BC) reaction products of chlorobenezene (CB) in the molar ratio (BC/CB) of 1: 15 at 80 ºC(٣٠ min)

Conclusion

Many ferrite materials were synthesized from simple salts precursors. The synthesized ferritematerials include Iron ferrite(Fe-Fer), Zinc ferrite(Zn-Fer)), Nickel ferrite(Ni-Fer),Cadmium ferrite(Cd-Fer) and Vanadium(V-Fer). The synthesized ferrite materials were applied in benzylationof chlorobenzene with benzyl chloride as the alkylating agent. This reaction was studied at differentconditions such as temperature, molar ratio, type of catalyst, the weight of the catalyst, reusability testand leaching test. In general, the ferrite catalysts showed very high catalytic performance forbenzylation of chlorobenzene, especially Zn-Fer and Ni-Fer.

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