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3.3.2.1 Research Paper Published in UGC Care Listed Journals

Application of ICT Based Chemistry: Through Virtual Practical Practises (VPP)

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Abstract

This present study view of apply information and communication technologies (ICT) into the faculty, Teaching and learning of chemistry. Studies includes, investigate students ICT skill in Chemistry in exacting and in science. In universal set up, ICT-based learning environment play a important role in education. While this seems to be true as an overall measurement, the future is affected by innovation, rapid moving, and in many ways random, This study talk about and exemplifies visualization in laboratories such as molecular modeling, data collection, and presentation¹. We focus also on ICT use chemistry via World Wide Web (WWW) and stereochemical virtual reality as well as the role of ICT for developing higher-order thinking skills such as inquiry chemistry using ICT is introduced including some recommendations from survey conducted with under graduate students. The survey and views were based on Virtual chemical Reaction, Interaction sessions and Organic, Inorganic Practical can also be done and understand by virtually and Virtual Practical Practices (VPP).

Keywords: Virtual Chemistry, Information and communication technologies (ICT), Organic Chemistry, Virtual Practical Practices (VPP).

INTRODUCTION:

In chemistry teaching the use of computers has been usual for a long time. Nevertheless, only a diffident part of the natural capability of modern computers is used for the solving of chemical problems and understanding the reaction and bonding²⁻⁵. Numerical

problems are solved, such as the ones encountered in quantum chemistry, and in the collection and evaluation of experimental data, or large sets of data are subjected to storage and retrieval operations. While the actual processes taken place during any chemical change can also be observed by putting the all starting materials and reagents together visually as shown in **fig 1**.

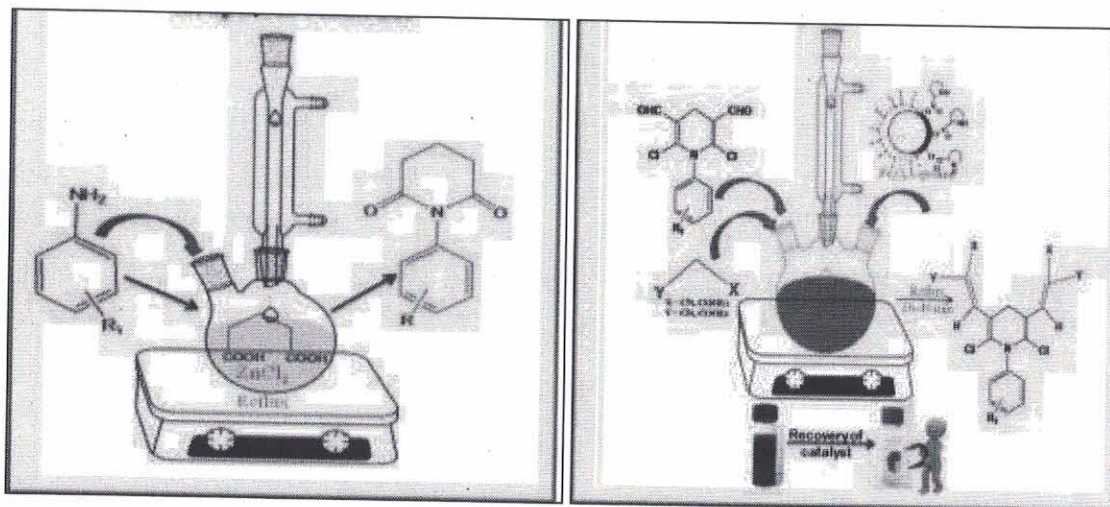


Figure 1: Reaction Set up virtually

The challenge to solve chemical spectra and problems by algorithms which create human aptitude in the sense of decision process and deductive thought was felt at a rather early period. It led to studies in a direction which is now associated with the term “artificial intelligence”. This growth began more than 10 years ago with computer programs for the clarification of molecular structures from measured physicochemical data“] (e. g. mass spectra), and also with retrieval oriented computer assisted synthesis design[*]. In the latter type synthesis design programs, stored information on chemical reactions is used to generate the precursors of a given synthetic target molecule. Here the structural features of the target molecule are perceived and analyzed in order to determine which of the reactions in a library of stored known reactions may lead to the target. For such reactions the corresponding precursors of the target are generated⁶⁻¹⁰.

To understand the students interest we have make one survey regarding the classes was taken by the faculty the result of the observation as shown in result and discussion section.

Results and Discussion:

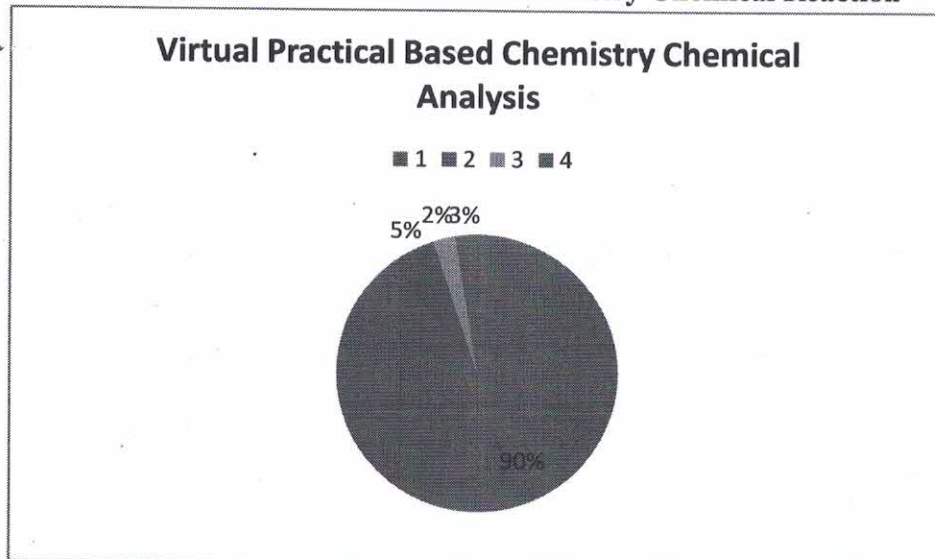
Table 1: Students Participated during ICT based study survey

Sr. No.	Students Code	Virtual Practical Based Chemistry								Virtual Theory Based Chemistry							
		Chemical Reaction				Chemical Analysis				Basic Concept				Theory Based			
		E	G	A	N.I.	E	G	A	N.I.	E	G	A	N.I.	E	G	A	N.I.
1.	SGPC1.	E				E				E				E			
2.	SGPC2.	E				E				E				E			
3.	SGPC3.	E				E				E				E			
4.	SGPC4.	E				E					G			E			
5.	SGPC5.	E				E				E				E			
6.	SGPC6.	E				E				E							N.I.
7.	SGPC7.	E					G			E				E			
8.	SGPC8.	E				E				E				E			
9.	SGPC9.	E				E				E				E			
10.	SGPC10.		G					A		E				E			
11.	SGPC11.	E				E				E				E			
12.	SGPC12.		G			E				E				E			
13.	SGPC13.	E				E				E				E			
14.	SGPC14.	E				E				E				E			
15.	SGPC15.	E				E				E				E			
16.	SGPC16.	E							N.I.	E				E			
17.	SGPC17.	E				E				E				E			
18.	SGPC18.	E				E				E				E			
19.	SGPC19.	E				E				E				E			
20.	SGPC20.	E				E				E				E			
21.	SGPC21.	E				E						A		E			
22.	SGPC22.	E				E				E				E			
23.	SGPC23.	E				E				E				E			
24.	SGPC24.				N.I.	E				E				E			
25.	SGPC25.	E				E				E					G		
26.	SGPC26.	E				E				E				E			
27.	SGPC27.			A		E				E				E			
28.	SGPC28.	E				E					G			E			
29.	SGPC29.	E				E						A			G		

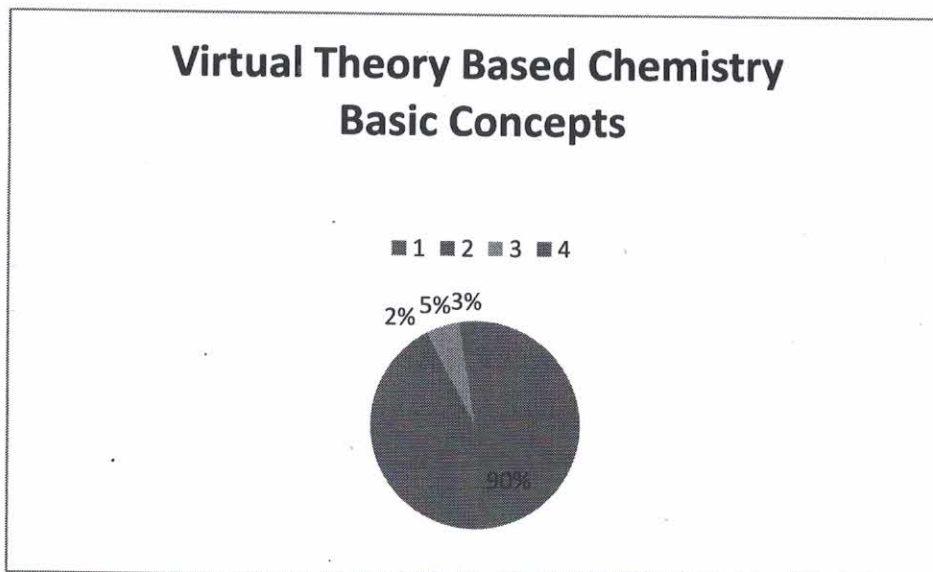
30.	SGPC30.	E				E				E								N.I.
31.	SGPC31.	E				E				E				E				
32.	SGPC32.	E				E				E				E				
33.	SGPC33.	E				E				E				E				
34.	SGPC34.	E				E				E				E				
35.	SGPC35.	E				E				E							A	
36.	SGPC36.	E					G			E				E				
37.	SGPC37.	E				E				E				E				
38.	SGPC38.	E				E				E				E				
39.	SGPC39.	E				E							N.I.	E				
	Total	35	2	1	1	35	2	1	1	35	1	2	1	34	2	1	2	

E= Excellent, G= Good, A= Average, N.I. = Not Interested

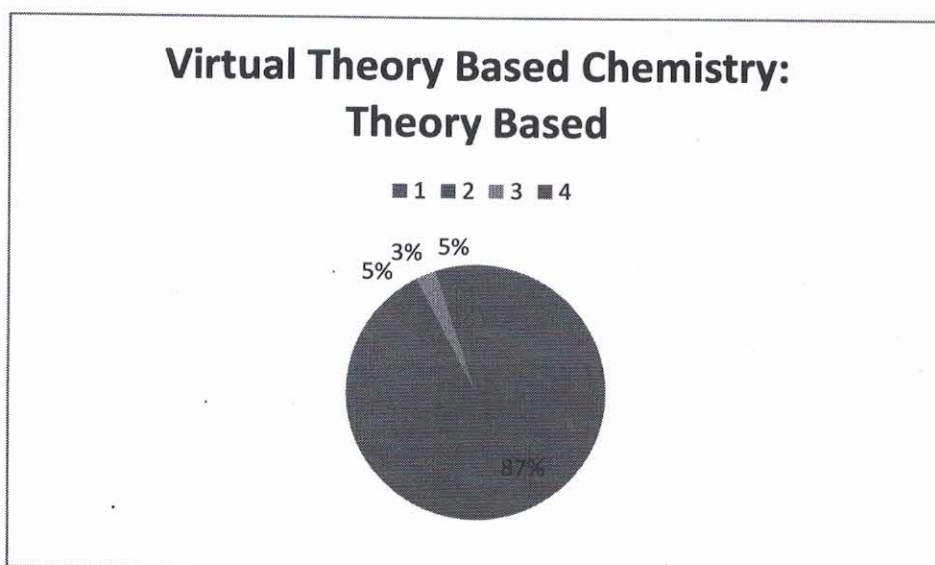
Pai Chart 1: Virtual Practical Based Chemistry Chemical Reaction



Pai Chart 2: Virtual Practical Based Chemistry Chemical Analysis



Pai Chart 3: Virtual Theory Based Chemistry Basic Concepts



Pai Chart 4: Virtual Theory Based Chemistry

From the above table 1 and Pai Chart most of students are interested to study the chemical reaction through ICT based teaching and it also increases their understanding level in chemical bonding and reactions.

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3.3.2.1 Research Paper Published in Peer Reviewed and Referred Journals

Knoevenagel Condensation of Substituted Aldehydes and Active Methylene Compounds Using Ferrite Magnetic Nanoparticles

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Abstract:

Conducting the reactions, using heterogeneous catalysts should compensate some of drawbacks observed in previously reported reactions. In this kind of reaction, the catalyst can be separated by filtration. Magnetite nanoparticles (Fe_3O_4) have attracted much attention in the past decade, due to their unique features including low preparation cost, high thermal as well as mechanical stability and adaptability for large-scale production. Magnetite nanoparticles (Fe_3O_4) can be easily separated from reaction mixture by using an external magnet. We have demonstrated a very simple and highly efficient method for the Knoevenagel reaction of aromatic aldehydes with various active methylene containing compounds to give Knoevenagel products in good to excellent yields at refluxed temperature. In the above research we suggest that the present method of environmentally benign Fe_3O_4 displace all other methods that use various homogeneous catalysts and that are performed at high temperature.

Keywords: Magnetite Nanoparticles, Knoevenagel Condensation, Active Methylene Compounds, Heterogeneous Catalysts

INTRODUCTION:

Today organic synthesis based on magnetic nanomaterial's are found a major role in

many fields including industrial procedure, biotechnology, biomedicine, environmental remediation and especially catalysis[1-2]. Most of these reactions are generally carried out in organic solvents, with a few aqueous phase organocatalytic processes as recent exceptions[3]. Although water is an environmentally benign solvent[4]. The use of environmentally benign solvents like water[5] and absent of organic solvent reactions represent very effective green chemistry[6] methods from economical as well as synthetic point of view[7]. They not only reduce the load of organic solvent but also improve the speed of many organic reactions. Therefore efforts have been made to carry out the Knoevenagel condensation in aq. medium [8]. It was found that the Knoevenagel condensation reaction of aromatic aldehydes with malononitrile or ethyl cyanoacetate take place in aq. medium[9]. The separation and recycling of the catalyst is highly favorable because catalysts are very expensive.

Surface reform via functional group immobilization provides unique prospect to engineer the interfacial properties of solid substrates while holding their mechanical strength and basic geometry. Surface engineering can be attained either by physically adsorbing or chemically creating functional groups onto a suitable matrix. Chemical bonding of functional groups offers a unique advantage since the implanted molecule detachment is prevented due to strong covalent bonding of the molecule to the substrate. Immobilization of molecules on organic/inorganic support has been extensively studied [10] with much attention given to establishment of new covalent bond on the desired surface [11]. There are wide reports [12-13] on immobilization of modifiers like chelate forming organic reagents, polymers, natural compounds, metal salts some microorganisms on solid mediums like ion-exchange resins, cellulose, fibers, sand, clay, zeolites, polymers, metal oxides, activated carbon and highly dispersed silica. Such researches of immobilization of groups or compounds depend on substitution reaction between the surface of the supporting material and the modifiers. An active adsorbent should have good adsorption capacity, chemical stability under experimental

condition and especially high selectivity [14]. Among the different adsorbents, silica gel particularly restrained with various organic compounds with metal chelating ability has received great attention [15-20]. Immobilization of organic functional groups on a siliceous surface has been effectively employed to produce ranges of modified silica. In this process, organic reagent or manufactured organic molecule having the preferred organic functional group is directly attached to the support or to the original chain bonded to the support via sequence of reactions to increase the main chain, where other basic centers can be added to ensure the improvement of a specific adsorption [21].

Conducting the reactions by using heterogeneous catalysts had reduced some of drawbacks observed in previously reported reactions. In this type of reactions, the catalyst can be recovered by filtration and it can be reuse for the next cycle. However, it is worthy to mention in spite of several advantages experienced practically in using of heterogeneous catalysts, due to the nanosized particles used, few limitations to the sustainability are observed [20]. To get around these problems, the use of a heterogeneous catalyst which can be separated practically other than filtration is desirable. Magnetite nanoparticles (Fe_3O_4) have attracted much attention in the past decade due to their unique features including low preparation cost, high thermal and mechanical stability and adaptability for large scale production. In addition, their paramagnetic nature allows their facile and effective separation from the reaction mixture, without using standard filtration, required in separation of heterogeneous catalysts. Magnetite nanoparticles (Fe_3O_4) can be easily separated from reaction mixture by using Just an external magnet [21]. Thus, in recent years, nano- Fe_3O_4 [22] has attracted a great attention as heterogeneous catalyst [23] due to its simple handling, easy recovery by an external magnet [24, 25]. Magnetic nanoparticles (MNPs) have emerged as viable alternatives to conventional materials as robust, readily available, oxidative stability, biological compatibility and high catalytic activities in various organic transformations [26–31]. The nano particles enhance the exposed surface area of the active constituent of the

catalyst [32, 33], thereby increasing the contact between reactants and catalyst dramatically [34–38] these nano-catalysts bridge the gap between homogeneous and heterogeneous catalysis [39], thus preserving the desirable attributes of both systems [40, 41].

We have carried out reaction of various substituted benzaldehyde with acyclic active methylene compounds (malononitrile, ethyl cyanoacetate, ethyl acetoacetate) and cyclic active methylene compounds (barbituric acid and thiobarbituric acid) in presence of ferrite heterogeneous catalyst as shown in **scheme 1**

Experimental

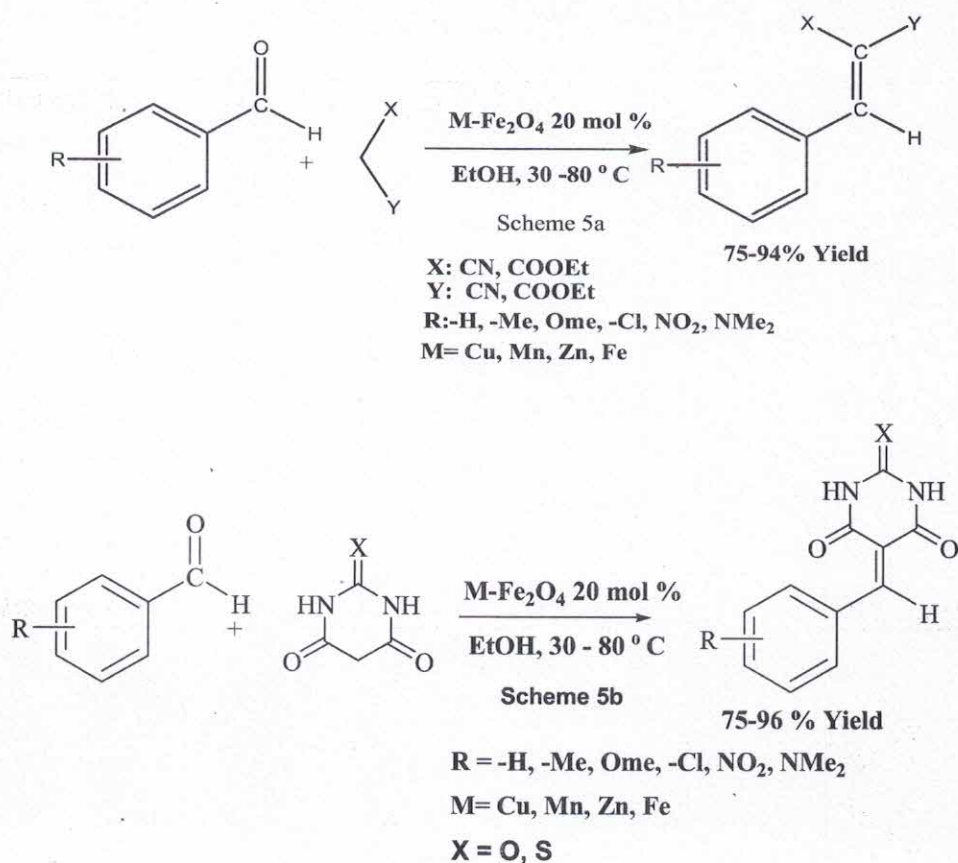
Material and Methods:

Preparation of magnetic Fe₃O₄ nanoparticles (MNPs):

The mixture of FeCl₃·6H₂O (5.838 g, 0.022 mol) and FeCl₂·4H₂O (2.147 g, 0.011 mol) were dissolved in 100 mL of deionized water in a round bottom flask (250 mL) at room temperature under stirring. Thereafter, 10 mL of aq. NH₃ solution (32%) was then added into mixture within 40 min with vigorous mechanical stirring. Finally the black precipitate solid was collected by magnetic decantation, washed with distilled water until solution becomes neutral, and then washed with ethanol two times. After the performed of procedure the magnetic nano materials have been characterized using an Infrared spectroscopy and the structure of magnetic catalysts was determined by X-ray diffraction (XRD) study. The crystal size of catalyst was checked by scanning electron microscope (SEM).

General procedure:

We have carried out reaction of various substituted benzaldehyde with acyclic active methylene compounds (malononitrile, ethyl cyanoacetate, ethyl acetoacetate) and cyclic active methylene compounds (barbituric acid and thiobarbituric acid) in presence of ferrite heterogeneous catalyst as shown in **scheme 5**.



Scheme-1 M-Ferrite catalyst Knoevenagel condensation (a&b) .

Results and Discussion

We have made an effort to develop a catalytic system that would address the limitations of the earlier reported Knoevenagel reactions. During the preliminary studies benzaldehyde (1a) and malononitrile (2a) used as a model system. A sequence of experiment were conducted to optimize a variety of reaction parameters, such as the type of catalyst, catalyst quantity, solvent, temperature and time (Table 1). Initially we developed the paramount magnetically separable catalysts, MFe_2O_4 ($M=Fe^{2+}$, Zn^{2+} , Mn^{2+} and Ni^{2+}), have been synthesized by thermal decomposition and were consequently screened for the model system of reaction as shown in **scheme 5**. Among the catalysts examined, Fe_3O_4 was found to be the best, providing excellent yields of the desired product 3a (Table 1, entries 1-5). We further studied catalysts concentration ranging from 5 to 20mol% rises the yield of product 3a up to 94%, a further increase of catalyst concentration to 25mol% did not improve the yield

of 3a (Table 1 entries 1,2,6). As the solvent have an impact on the overall process, the effect of various solvents (Table 1 entries 2,7-11,13) were examined; the best results was obtained with ethanol which afforded 3a in 94% yield (Table 1 entry 2). We also studied the effect of the temperature and found that the 3a obtained good yield at room temperature for complete consumption of aldehyde. (Table 1 entry 2,12). After optimizing the reaction conditions, we explore the substrate scope of the ferrite catalyzed Knoevenagel condensation of substituted aldehydes with acyclic active methylene compounds (malononitrile, ethyl cyanoacetate, ethyl acetoacetate) and cyclic active methylene compounds (barbituric acid and thiobarbituric acid) for the synthesis of styrene derivatives containing different functional groups. We observed that electron donating as well as electron withdrawing substituents provide remarkable yield of products. Satisfyingly this protocol endured a range of common functional groups such as alkyl, ether, halogen and nitro groups irrespective of the positions. The results of these reactions are summarized in Table 2.

In order to make our catalytic system more economical, we focused on the reusability of Fe_3O_4 catalysts in this condensation reaction. As shown in Table 3, the catalysts shown surprising activity in all three recycles. The completion of the reaction was monitored by TLC. Followed by touching the external magnet to wall of the round bottom flask and the reaction mixture was decant in the small beaker, washed the catalyst with ethanol (3×5ml) and dried it for 1hr at 120°C in oven, then the catalyst was used directly in the next cycle. The catalyst was recycled three times and gives constant yields.

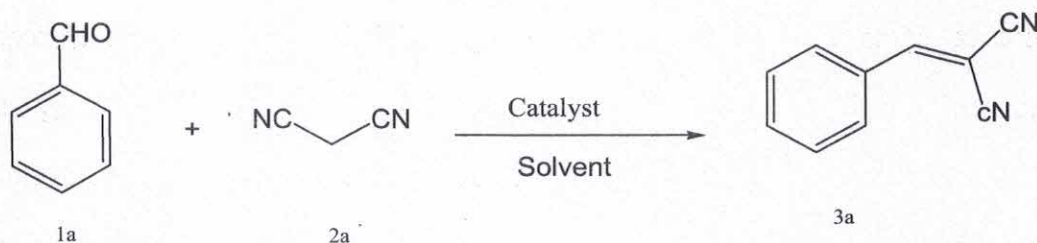
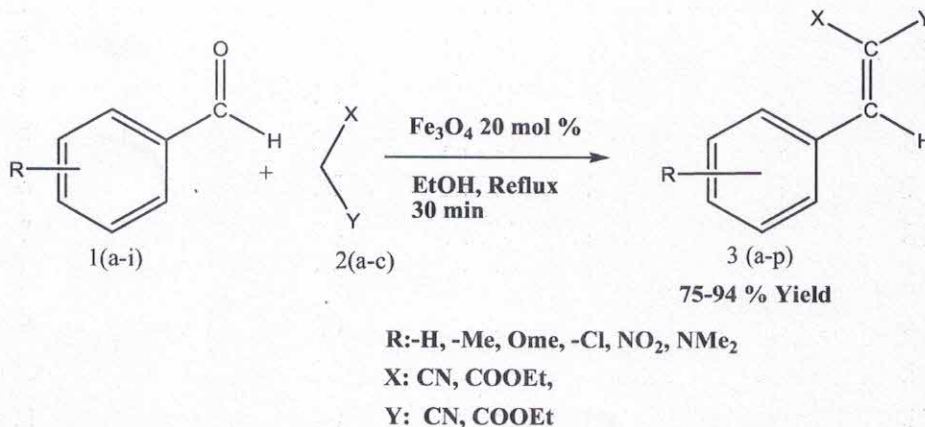


Table 01: The reaction parameters study

Entry	Catalyst	Catalyst (mol%)	Solvent	Temp (°C)	Time (min)	Yield (%)
1	--	--	EtOH	Reflux	120	19
2	Fe ₃ O ₄	20	EtOH	Reflux	30	94
3	ZnFe ₂ O ₄	20	EtOH	Reflux	30	85
4	MnFe ₂ O ₄	20	EtOH	Reflux	30	88
5	NiFe ₂ O ₄	20	EtOH	Reflux	30	86
6	Fe ₃ O ₄	25	EtOH	Reflux	30	94
7	Fe ₃ O ₄	20	ACN	Reflux	30	87
8	Fe ₃ O ₄	20	H ₂ O	Reflux	30	46
9	Fe ₃ O ₄	20	MeOH	Reflux	30	64
10	Fe ₃ O ₄	20	CHCl ₃	Reflux	30	26
11	Fe ₃ O ₄	20	PEG-400	80	30	43
12	Fe ₃ O ₄	20	EtOH	60	30	81
13 ^c	Fe ₃ O ₄	20	--	80	30	59

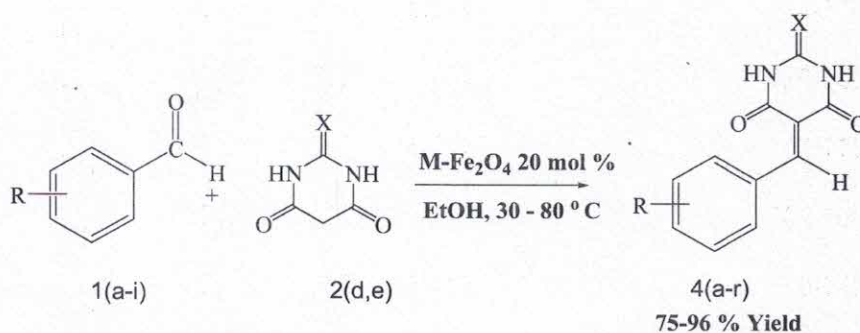
^aReaction conditions:Benzaldehyde (1mmol), Malononitrile (1 mmol), Solvent (3 mL), ^bIsolated yield, ^cNeat reaction**Table 2: Substrate study catalyzed by Fe₃O₄**

Entry	Aldehyde (-R)	X	Y	Product	Yield (%)	M.P. (°C)
1.	-H	CN	CN	3a	94	82-84
2.	-H	CN	COOEt	3b	91	47-49
3.	-H	COOEt	COOEt	3c	90	Oil
4.	4-Cl	CN	CN	3d	89	162-164

5.	4-Cl	COOEt	COOEt	3e	90	84-86
6.	2-Cl	CN	CN	3f	82	96-98
7.	2-Cl	CN	COOEt	3g	86	Oil
8.	4-NMe ₂	CN	CN	3h	84	186-188
9.	4-NMe ₂	CN	COOEt	3i	86	124-126
10.	4-NO ₂	CN	CN	3j	94	158-169
11.	4-NO ₂	CN	COOEt	3k	93	168-170
12.	3-NO ₂	CN	CN	3l	90	104-106
13.	2-NO ₂	CN	CN	3m	90	140-142
14.	3-OMe	COOEt	COOEt	3n	80	240-242
15.	3,4-di OMe	CN	CN	3o	86	142-144
16.	3,4-di OMe	CN	COOEt	3p	82	156-158

^aReaction conditions:

Aldehyde (1mmol), acyclic active methylene compound (1 mmol), Ethanol(3 mL), ^bIsolated yield,



R = -H, -Me, -OMe, -Cl, NO₂, NMe₂

X = O, S

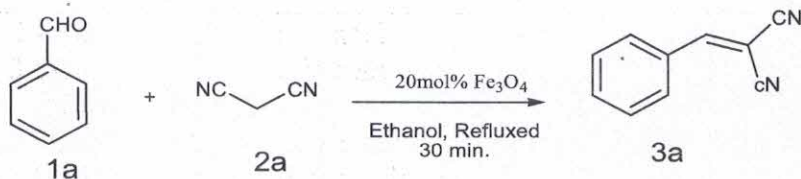
Entry	Aldehyde (-R)	Active methylene	Product	Yield (%)	M.P. (°C)
1	-H	Barbituric acid	4a	96	270-272
2	2-Cl	Barbituric acid	4b	90	220-222
3	4-Cl	Barbituric acid	4c	93	232-234
4	4-NMe ₂	Barbituric acid	4d	88	276-278
5	4-NO ₂	Barbituric acid	4e	96	>290
6	3-NO ₂	Barbituric acid	4f	92	256-258
7	2-NO ₂	Barbituric acid	4g	92	258-260

8	3-OMe	Barbituric acid	4h	93	268-270
9	3,4-di-O Me	Barbituric acid	4i	90	
10	-H	Thiobarbituric acid	4J	96	271-272
11	2-Cl	Thiobarbituric acid	4k	90	234-236
12	4-Cl	Thiobarbituric acid	4l	94	288-290
13	4-NMe ₂	Thiobarbituric acid	4m	90	254-256
14	4-NO ₂	Thiobarbituric acid	4n	96	240-242
15	3-NO ₂	Thiobarbituric acid	4o	92	246-248
16	2-NO ₂	Thiobarbituric acid	4p	93	240-242
17	3-OMe	Thiobarbituric acid	4q	90	236-238
18	3,4-di-O Me	Thiobarbituric acid	4r	89	

^aReaction conditions: Aldehyde (1mmol),cyclic active methylene compound (1 mmol), Ethanol(3 mL),

^bIsolated yield,

Table 3: Recycling of Catalyst



Entry	Run No.	Yield (%)
1	1 st	94
2	2 nd	88
3	3 rd	76

After the performed of synthesis procedure of the magnetic nano materials have been characterized using an Infrared spectroscopy and the structure of magnetic catalysts was determined by X-ray diffraction (XRD) study. The crystal size of catalyst was checked by scanning electron microscope (SEM).

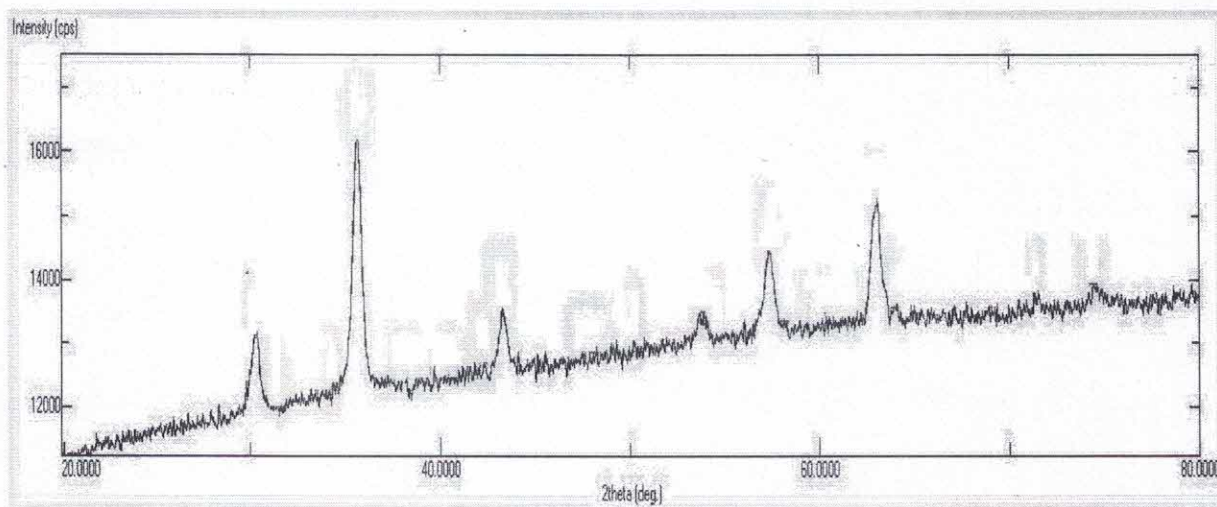


Figure 1: X-ray diffraction (XRD) study of ferrite catalyst

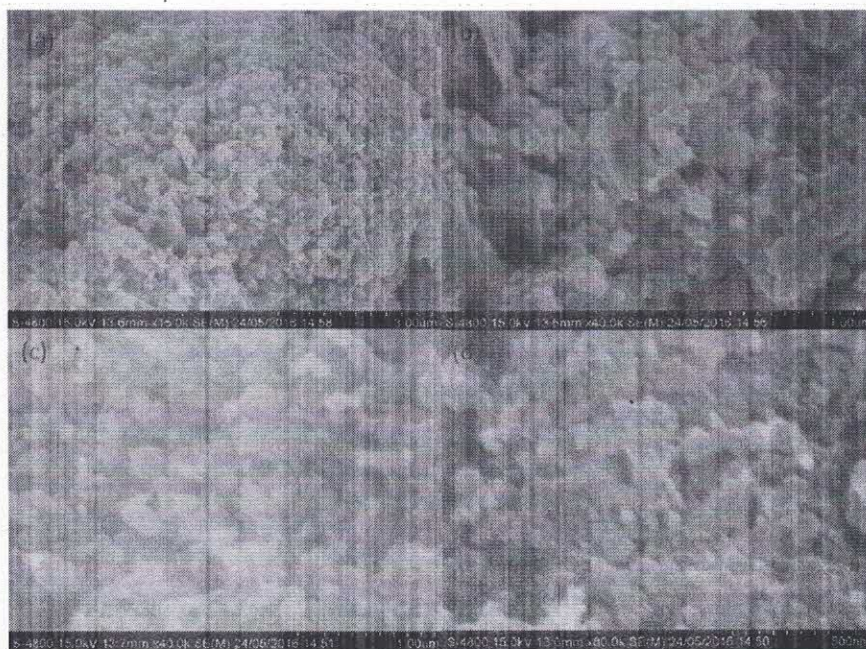


Figure 2: Scanning Electron Microscope (SEM) images of ferrite catalyst

Synthesis of styrene compounds:

A mixture of benzaldehyde (1 mmol), malononitrile (1 mmol), Fe_3O_4 (20 mol%) in ethanol (3 mL) was heated at reflux for 30 min. Progress of the reaction was monitored by TLC. The catalyst was recovered by simple magnetically decantation of reaction mixture by pouring in to ice water and the product was filter and purified by aq. ethanol. The recovered catalyst was washed with ethanol and dried in oven. The catalyst is

ready for next cycle of reaction.

Spectral data of some selected compounds:

1) 2-(2-Chlorobenzylidene)malononitrile (3d)

M.P.: 94-96°C. ^1H NMR (DMSO- d_6) δ : 8.295(s, 1H), 8.205(d, 1H, $J = 8.0\text{Hz}$), 7.576(d, 2H, $J=3.6\text{Hz}$), 7.495 – 7.435(m, 1H); C^{13} : 156.05, 136.35, 135.04, 130.72, 129.51, 129.07, 127.80, 113.22, 111.91, 85.81. IR (cm^{-1}): 3055, 2927, 2222, 1907, 1587, 756, 619;

2) 2-(4-chlorobenzylidene) malononitrile (3f).

M.P 162-164°C ; ^1H NMR (DMSO- d_6) δ : 7.880(d, 2H, $J=8.4\text{Hz}$), 7.760(s, 1H), 7.545(d, 2H, $J=8.4\text{Hz}$); C^{13} : 158.30, 141.18, 131.86, 130.09, 129.28, 113.45, 112.35, 83.37. IR: 3030, 2227, 1955, 1558, 779, 617

3) 2-(2-nitrobenzylidene)malononitrile (3m).

M.P 140-142°C ; ^1H NMR (DMSO- d_6) δ : 8.474(s, 1H), 8.393 - 8.369(m, 1H), 7.931-7.891(m, 1H), 7.855-7.816(m, 2H), C^{13} : 158.83, 146.80, 134.98, 133.44, 130.49, 126.72, 125.88, 112.24, 110.98, 88.55. IR: 3047, 2239, 1975, 1591, 1523, 1440

4) 2-(3,4-dimethoxybenzylidene)malononitrile (3o).

M.P.: 142-144°C ; ^1H NMR (DMSO- d_6) δ : 7.683 (t, 2H, $J = 2.0$ & 12.0Hz), 7.399(q, 1H, $J=2.4$ & 6.0 Hz), 7.283(s, 1H), 4.003(s 3H), 3.953(s, 3H); C^{13} : 159.15, 154.28, 149.56, 128.22, 124.29, 114.42, 113.59, 111.10, 11, 0.78, 78.45, 56.34, 56.09. IR: 2933, 2833, 2218, 1909, 1467, 1251, 1147

5) (Z)-ethyl 2-cyano-3-(3,4-dimethoxybenzylidene)acrylate (3p).

M.P. 156-158°C ; ^1H NMR (DMSO- d_6) δ : 8.162 (s, 1H), 7.808(s, 1H), 7.482 (d, 1H, $J = 7.6$ Hz), 6.955(d, 1H, $J = 7.6$ Hz), 4.377 (q, 2H, $J = 7.2$ Hz), 3.900(s, 6H), 3.400(t, 3H, $J= 7.2$ Hz); C^{13} : 163.11, 154.70, 153.68, 149.28, 127.89, 124.61, 116.36, 111.65, 110.95, 99.38, 62.46, 56.15, 56.05, 14.21. FT-IR: 3003, 2845, 2222, 1928, 1710, 1512, 1159, 1097

Characterization of cyclic active methylene compounds:

1) 5-benzylidenepyrimidine-2,4,6(1H,3H,5H)-trione(4a).

M.P. 270-272°C ; ¹H NMR (DMSO-d₆) δ: 11.735(bs,2H), 7.913(t,1H, J =6.8 &1.6 Hz), 7.615 (t,1H , J= 6.8 & 7.6Hz),7.180(t,1H, J= 7.6 Hz), 7.075(t,1H, J= 7.2 Hz), 7.015(d,2H, J = 8.0 Hz), 5.946(s,1H); C¹³: 193.74, 173.30, 163.50, 142.89, 136.64, 135.07, 133.89, 129.96, 129.63, 128.61, 128.17, 126.99, 125.44, 96.35, 31.06.FT-IR: 3512, 3313,3074, 2845, 1880, 1701, 1581,1438

2) 5-(3-methoxybenzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione(4h)

M.P. 268-270°C ; ¹H NMR (DMSO-d₆) δ: 11.407(s, 1H), 11.256(s, 1H), 8.259(s, 1H), 7.845(t, 1H, J = 2.0Hz); 7.611(q, 1H, J = 7.2,0.8Hz &.0.4Hz;), 7.395(t, 1H, J = 8.0 Hz), 7.142 – 7.117(m, 1H,) 3.797(s,3H);. C¹³: 163.87, 162.09, 159.08, 154.98, 150.64, 134.31, 129.59, 126.55, 119.74, 118.91, 118.07,55.68. IR:3518, 3458, 3007, 2828, 1938, 1660, 1570, 1444, 1163

3)5-(2-chlorobenzylidene)-dihydro-2-thioxopyrimidine-4,6(1H,5H)-dione (4k)

M.P.: 234-236°C ;¹H NMR (DMSO-d₆) δ: 11.491(s, 1H), 11.272(s, 1H), 8.292,(s, 1H), 7.747 (t, 1H, J= 6.8 & 0.8 Hz;), 7.556, (q,1H, J= 1.2Hz & 6.8Hz;), 7.497 – 7.456, (m, 1H), 7.392 - 7.352, (m,1H);C¹³: 163.12, 161.38, 150.69, 150.17, 133.64, 132.74, 132.44, 132.40, 129.35, 126.80, 122.26.FT-IR: 3633, 3388, 3076, 1718, 1583, 1215, 1049,725, 642

4)5-(3-methoxybenzylidene)-dihydro-2-thioxopyrimidine-4,6(1H,5H)-dione (4q) M.P.: 236-238°C ;

¹H NMR (DMSO-d₆) δ: 12.477(s,1 H), 12. 357(s,1H), 8.271(s, 1H), 7.892(s, 1H), 7.676 -7.657(d,1H, J= 7.6Hz),7.430 7.390(m,1H, J = 8.0Hz), 7.172-7.147, (m,1H), 3.803 (s, 3H);C¹³: 179.02, 162.18, 159.94, 159.12, 155.88, 134.29, 129.68, 126.92, 119.80, 119.45, 118.31, 55.72.IR: 3485, 3070, 2904, 1944, 1701,1651, 1548,1228, 1151, 1047

5)(3,4-dimethoxybenzylidene)-dihydro-2-thioxopyrimidine-4,6(1H,5H)-dione (4r) M.P

°C, ¹H NMR (DMSO-d₆) δ: 12.403- 12.300(d, 2H), 8.438(d, 1H, J= 1.6Hz), 8.275(s,1H), 7.969 (t, 1H, J= 1.2 & 7.2 Hz), 7.157(q, 1H, J = 8.0 & 9.2 Hz), 3.830(s,6H); C¹³: 191.86,

178.65, 162.76, 160.60, 156.97, 154.70, 154.66, 149.63, 148.35, 132.84, 130.09, 126.60, 125.91, 117.43, 115.79, 111.74, 111.69, 109.87, 56.42, 56.35, 55.98, 55.93. IR: 3577, 3363, 3138, 2926, 1923, 1712, 1685, 1535, 1201, 1018

Conclusion:

We have demonstrated a very simple and highly efficient method for the Knoevenagel reaction of aromatic aldehydes with various active methylene containing compounds to give Knoevenagel products in good to excellent yields at refluxed temperature. In the above research we suggest that the present method of environmentally benign Fe_3O_4 displace all other methods that use various homogeneous catalysts and that are performed at high temperature.

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