

## The zinc chromium ferrite magnetic nanoparticles ZnCrFeO<sub>4</sub>: An efficient catalyst for acetylation of alcohols, phenols and amines under solvent-free conditions

Nahid Rasouli\*, Maryam Movahedi, Elaheh Aghabeikzadeh Naeini

Department of Chemistry, Payame Noor University, P.O. BOX 19395-3697 Tehran, Iran

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### Abstract

In this study, the zinc chromium ferrite magnetic nanoparticles ZnCrFeO<sub>4</sub> are synthesized via sol-gel method and characterized by X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The XRD analysis showed that ZnCrFeO<sub>4</sub> has single-phase cubic structure. The synthesized ZnCrFeO<sub>4</sub> has been used as an efficient catalyst for acetylation of alcohols, phenols and amines with acetic anhydride under mild and solvent free conditions. The ZnCrFeO<sub>4</sub> catalyst can be readily removed using an external magnet and no obvious loss of activity was observed after three consecutive runs. Also, the effect of time, amount and type of catalyst were investigated.

**Keywords:** Acetylation; catalyst, magnetic; solvent free.

### Introduction

In the multi-step organic syntheses, the protection and deprotection of organic functional groups are important. The choose of functional group transformation is based on considering the simplicity of the reaction, high yields of the desired products, short reaction times along with low cost process and an easy work-up [1-3]. The acetylation of alcohols, phenols and amines is one of the most important and frequently used transformations in organic synthesis, especially in the synthesis of natural compounds, biologically active compounds and polyfunctional molecules such as nucleosides, carbohydrates, flavanones, naphthoquinones, pesticides and steroids [4,5]. These reactions are carried using acid chloride or

anhydrides [6,7] as acetylating agent and catalysts such as AlCl<sub>3</sub>, BF<sub>3</sub>, TaCl<sub>5</sub> [8], inorganic acids [9] and organic bases [10] that many of them are explosive, moisture sensitive and expensive. Also, many of these catalytic methods were carried out under difficult conditions such as high acidic, high temperatures, stoichiometric amount of catalyst, long reaction times and low yields. Another disadvantage is that most of these catalysts need organic solvents as media for reaction. The development of green synthetic protocols in order to reduce or eliminate the use and generation of hazardous substances constitutes one of the major challenges for chemists. In particular, there has been an increasing demand for efficient organic solvent-free synthetic process,

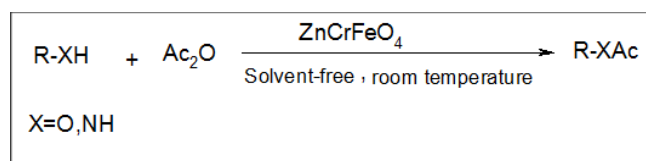
\*Corresponding author: Nahid Rasouli

Tel: +98 (31) 32608028, Fax: +98 (31) 32608030

E-mail: n.rasouli@pnu.ac.i, n.rasooli55@yahoo.com

however; the ideal approach would be carrying out reaction in total absence of solvent, thus gaining the great advantage of low cost, low environmental impact and low toxicity in handling [11,12]. Therefore, for the development of greener processes, solvent free reactions and easy handling solid acid catalysts are desired [13-19]. In this regard, the discovery of a new and efficient catalyst with high catalytic activity, short reaction time, recyclability and simple work-up for the acetylation reactions under mild conditions and green chemistry is of main interest. Nanoparticles due to their high surface area have received increasing attention [20]. Nevertheless, tedious recycling of nano catalysts *via* filtration and inevitable loss of solid nano catalysts during the separation process have strongly limited their applications. So, much attention has been paid to the utilization of magnetic nanoparticles as reactive and easily recycled catalysts using external magnetic field [21]. In recent years, transition metal mixed oxides with spinel structure have attracted considerable attention as promising catalytic materials for organic transformations due to their high thermal and hydrothermal stability and relatively low cost compared with their noble metal counterparts [22,23]. The spinels (general formula  $A^{2+}B_2^{3+}O_4$ ) represent a class of materials, where the oxide anions arranged in a cubic close-packed lattice and the cations  $A^{2+}$  and

$B^{3+}$  occupying some or all of the octahedral and tetrahedral sites [24-26]. A and B can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminum, chromium, cobalt and silicon or can be the same metal under different charges. Spinel ferrites are commercially important materials because of their excellent structural, magnetic and electrical properties [27,28]. Ferrite spinels such as  $Fe_3O_4$  and  $\gamma-Fe_2O_3$  have been used as catalysts, but  $Fe_3O_4$  is reactive to acidic and oxidative environments [29] and  $\gamma-Fe_2O_3$  is not thermally stable [30]. Compared to the previous display,  $ZnCrFeO_4$  as ferrite spinel has high chemical stability and is used in various fields [31]. To the best of our knowledge, no previous report was described using  $ZnCrFeO_4$  as catalyst for the acetylation of alcohols, phenols and amines. Herein, for the first time, we have shown the application of  $ZnCrFeO_4$  magnetic nanoparticles as catalyst for the coupling of alcohols, phenols and amines with acetic anhydride. The synthesized  $ZnCrFeO_4$  exhibits good catalytic activity with an advantage of simple and fast catalyst recyclability by external magnet. The catalyst could be reused up to three run without loss of catalytic activity. Notably, the reaction proceeds under low catalyst and acetic anhydride loading, solvent free condition at room temperature.



**Scheme 1.** Acetylation reactions of phenols, alcohols and amines using  $ZnCrFeO_4$  nanoparticles

## Experimental

All of the chemicals were of high purity and used without further purification from Merck. The analysis of the prepared catalyst was performed by powder X-ray Diffraction (Holland Philips X-pert, X-ray diffractometer with Cu-K $\alpha$  radiation) and FT-IR using a Fourier transmission infrared spectrometer (JASCO FTIR- 4200, Japan) in KBr pellet and in the range of 4000 - 400 cm<sup>-1</sup>. The external morphology of the catalyst was characterized by scanning electron microscopy (JEOL JEM-3010 SEM). The characterization of the products were carried out by gas chromatography Perkin Elmer, GC Clarus 400 and <sup>1</sup>H NMR spectra were obtained on a Bruker DRX-400.

## Preparation of ZnCrFeO<sub>4</sub> magnetic nanoparticles

The synthesis of ZnCrFeO<sub>4</sub> nanoparticles was followed by the reported method [32]. In this method, a mixture of 8.07 g of Fe (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O with 5.94 g of Zn (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 8.00 g of Cr (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O were taken in a 100 mL round bottom flask. These materials were mixed with 50 mL methanol as solvent and then ammonium hydroxide solution was added until the pH was adjusted to 9. After stirring the mixture for 20 min at 80 °C, stirring was continued at room temperature for 24 h. Finally, the obtained product was washed with

double distilled water several times and dried at 60 °C and then heated for 2 h at 900 °C.

## General procedure for acylation reaction

In a 50 mL test tube containing a magnetic bar was added phenol/alcohol/amine (1 mmol), acetic anhydride (1 mmol) and ZnCrFeO<sub>4</sub> (5 mol%) as catalyst. The reaction mixture was stirred at room temperature for 1 h. The reaction progress was monitored on thin-layer chromatography (TLC) and gas chromatography analysis. After completion of the reaction, the reaction mixture was diluted with dichloromethane and catalyst was separated from reaction mixture using strong magnet. The separated catalyst was washed with distilled water several times, then dried in oven and reused for another reaction. The reaction mixture was washed with saturated NaHCO<sub>3</sub> solution (15 mL) and the product was extracted with ethyl acetate and dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. All the obtained products are well known in the literature and were confirmed by gas chromatography by comparison with literature data.

## Results and discussion

### Structural and morphological study of ZnCrFeO<sub>4</sub> nanoparticles

The crystal structure and phase purity of the ZnCrFeO<sub>4</sub> have been investigated by XRD.

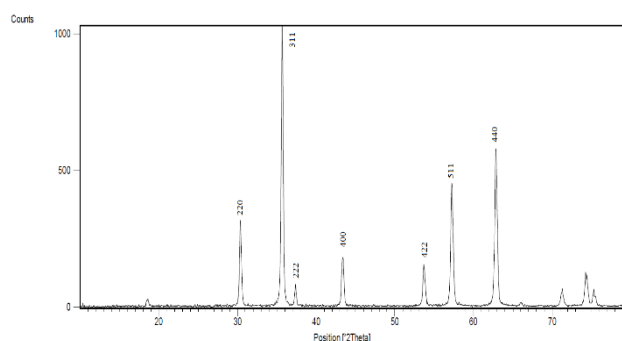
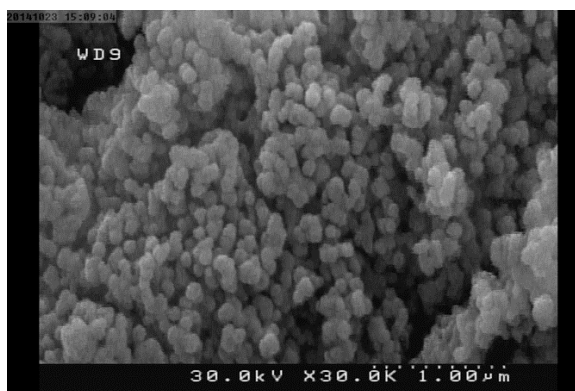


Figure 1. XRD pattern of synthesized ZnCrFeO<sub>4</sub>

Figure 1 shows characteristic peaks that occur at  $2\theta$  of 30.08, 35.36, 37.08, 43.08, 53.27, 56.93 and 62.44 which are marked by their corresponding crystallographic planes (220), (311), (222), (400), (422), (511) and (440), respectively. The XRD results confirmed that the  $\text{ZnCrFeO}_4$  (Cubic, JCPDS no. 430554) was obtained. Furthermore, no impurity peaks are detected, which confirms the phase purity of the synthesized sample. The crystallite size ( $D$ ) of the  $\text{ZnCrFeO}_4$  sample was estimated using Scherer's equation as follows [33]:

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

Where  $\lambda$  is the wavelength of X-ray and  $\beta$  is full width at half maximum of the peak at diffracting angle  $\theta$ . According to eq (1), the crystallite size of the synthesized  $\text{ZnCrFeO}_4$  was calculated about 48 nm. The SEM image reveals that the powder is composed of aggregated, extremely fine semi-spherical particles. This observation indicates that the  $\text{ZnCrFeO}_4$  powder is a crystalline aggregate of nanoparticles (Figure 2).



**Figure 2.** SEM images of fresh  $\text{ZnCrFeO}_4$

The FT-IR spectra shows the three principles absorption bands of  $\text{Fe}^{3+}-\text{O}^2$ ,  $\text{Cr}^{3+}-\text{O}^2$  and  $\text{Zn}^{2+}-\text{O}^2$  located at around the range of 410, 490 and 615  $\text{cm}^{-1}$ , respectively. The peaks observed at around 3415 and 1544  $\text{cm}^{-1}$  are ascribed due to the stretching and bending vibration modes of H–O–H of the free or absorbed water molecules on the surface of the  $\text{ZnCrFeO}_4$  [34]. The absence of the peaks at 1000–1300  $\text{cm}^{-1}$  and 2000–3000  $\text{cm}^{-1}$  in the samples confirmed that the O–H mode and C–O mode stretching mode of organic sources in the calcined samples is not present [35].

#### **Catalytic application of $\text{ZnCrFeO}_4$ nanoparticles**

The latest research on catalysis reaction has been focused on green and

environmentally being methods which avoid the use of volatile organic solvents, toxic reagents, high reaction conditions and time consuming processes [36]. Magnetic nanocatalysts have advantages such as large surface to volume ratio, low catalyst loading and easy separation by external magnet [37]. The catalytic activity of synthesized magnetically recoverable  $\text{ZnCrFeO}_4$  was investigated for the acetylation reaction using phenols, alcohols and amines with acetic anhydride under solvent free condition at room temperature (Scheme 1). At first, the reaction of phenol with acetic anhydride was chosen as a model reaction and effects of various parameters such as catalyst loading, catalyst type and time were studied at room temperature under solvent free

reaction. At the beginning, the reaction was carried out in absence of the catalyst but reaction did not proceed (Table 1, Entry 1).

**Table 1.** Optimization of reaction conditions<sup>a</sup>

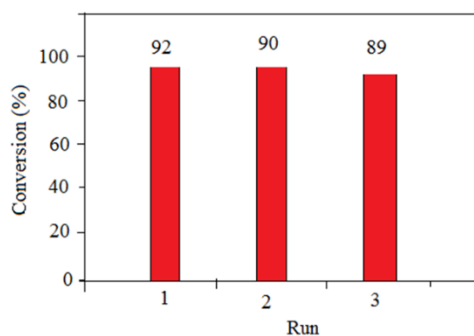
Entry	Catalyst	Catalyst (% mol)	Time (min)	Yield (%) <sup>b</sup>
Effect of catalyst loading				
1	No catalyst	0	60	-
2	ZnCrFeO <sub>4</sub>	1	60	14
3	ZnCrFeO <sub>4</sub>	3	60	49
4	ZnCrFeO <sub>4</sub>	5	60	92
5	ZnCrFeO <sub>4</sub>	10	60	89
Effect of time				
6	ZnCrFeO <sub>4</sub>	5	5	64
7	ZnCrFeO <sub>4</sub>	5	15	92
Effect of catalyst screening				
8	ZnO	5	60	56
9	Fe (NO <sub>3</sub> ) <sub>3</sub>	5	60	20
10	Fe (OAc) <sub>2</sub>	5	60	34
11	γ-Fe <sub>2</sub> O <sub>3</sub>	5	90	90

<sup>a</sup> Reaction condition: Phenol (1mmol), acetic anhydride (1 mmol), catalyst (5 mol%), RT.

<sup>b</sup>GC yield.

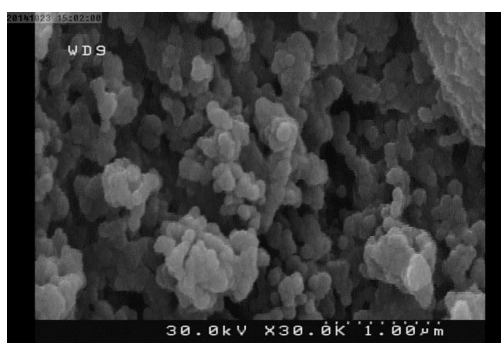
We applied the different catalyst loading using model reaction (Table 1, Entries 2-5). It was observed that 5 mol% of catalyst gives an excellent yield (92%) of the desired product (Table 1, Entry 4). Along with ZnCrFeO<sub>4</sub>, we also applied various catalysts such as Fe(OAc)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, ZnO [38] and γ-Fe<sub>2</sub>O<sub>3</sub> [39] to increase the reaction yield (Table 1, Entries 8-11). The results showed that the synthesized ZnCrFeO<sub>4</sub> exhibits good catalytic activity for the model reaction (Table 1, Entry 4). Also, we investigated the effect of reaction time and it was found that the high yield of the desired product was obtained within 15 min (Table 1, Entry 7). Studying the above optimized reaction conditions for acetylation reaction of phenol, we extended the scope of study for acetylation of various alcohols and amines (Table 2). The recyclability of

catalyst is a great advantage in the view from cost and environmental pollution. Here, we have investigated magnetic separation and reusability of the ZnCrFeO<sub>4</sub> for the acetylation reaction using phenol and acetic anhydride under solvent free conditions at room temperature. For this purpose, after completion of reaction, the reaction mixture was diluted with dichloromethane and the catalyst was removed by applying external magnet. Then, the catalyst was washed with distilled water and ethanol several times and used as catalyst for recyclability study. To study the deactivation and recyclability of the catalyst, three consecutive runs were carried out with ZnCrFeO<sub>4</sub> under optimized conditions. The results are shown in Figure 3 which indicated that there is no significant change in the activity of the catalyst up to 3 rd use.



**Figure 3.** Investigation of recyclability of the ZnCrFeO<sub>4</sub> as catalyst

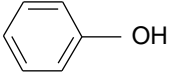
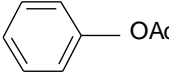
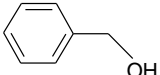
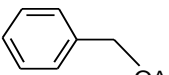
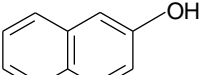
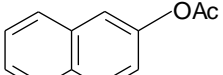
The Figure 4 displays SEM image of magnetically recycled ZnCrFeO<sub>4</sub> after three runs.


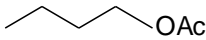


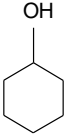
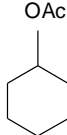
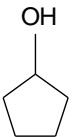
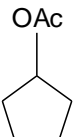
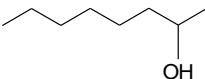
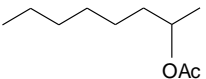
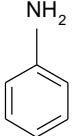
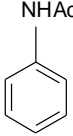
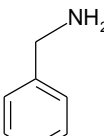
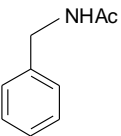
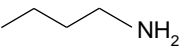

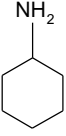
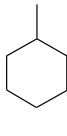


**Figure 4.** SEM images of magnetically recycled ZnCrFeO<sub>4</sub> after three runs

As seen from the figure that the catalyst can be recycled and reused without appreciable change in the catalyst morphology.

**Table 2.** Zinc chromium ferrite magnetic nanoparticles catalyzed acetylation of alcohols, phenols and amines using acetic anhydride under solvent free conditions<sup>a</sup>

Entry	Substrate	Product	Time (min)	Yield <sup>b</sup> (%)
1			15	91
2			30	73
3			15	78

4			15	97
5			15	70
6			30	99
7			15	91
8			15	97
9			15	95
10			15	85
11			15	90
12			15	95

<sup>a</sup>Reaction condition: substrate (1 mmol), acetic anhydride (1 mmol), ZnCrFeO<sub>4</sub> (5 mol%), RT, Solvent -free.

<sup>b</sup>GC yield

In order to show the advantage of the present catalytic system, we compared our results in the acetylation of benzyl

alcohol with those of some reported heterogeneous catalysts in the literature (Table 3).

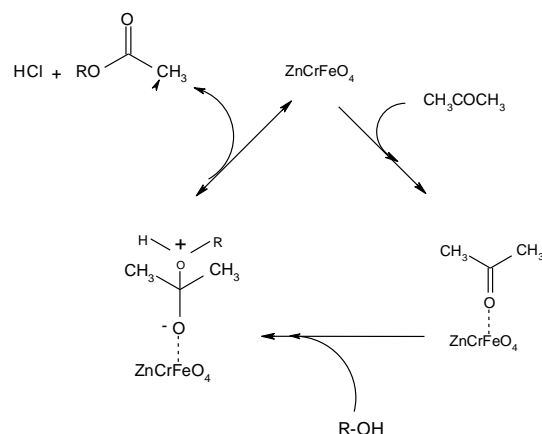
**Table 3.** Comparison of the result obtained for the acetylation of benzyl alcohol in the present work with those obtained by some reported heterogeneous catalysts

Entry	Catalyst	t (°C)	Time (min)	Ac <sub>2</sub> O(equiv.)	Yield (%)	Solvent	Ref.
1	Fe/SBA-15	40	25	3	98	-	[40]
2	ZPFe	40	15	2	91	-	[41]
3	Silica sulfamic acid	RT	15	2	93	-	[42]
4	ZnCl <sub>2</sub>	RT	180	1	63	-	[43]
5	ZrOCl <sub>2</sub> .8H <sub>2</sub> O	40	15	2	90	-	[41]
6	ZnAl <sub>2</sub> O <sub>4</sub> /SiO <sub>2</sub>	75	20	1	92	-	[44]
7	FER zeolite	75	120	1.5	91	-	[45]
8	ZnCrFeO <sub>4</sub>	RT	30	1	73	-	This work

From the reaction conditions, substrate/Ac<sub>2</sub>O molar ratio, reaction time, and product yield, it can be seen that the present catalytic system is superior. The advantages of the catalyst in this work in comparison with previously reported catalysts are low catalyst and Ac<sub>2</sub>O loading, solvent free condition, room temperature and easy and fast separation of catalyst by

external magnet. Also, the ZnCrFe<sub>2</sub>O<sub>4</sub> as catalyst has high chemical and thermal stability, no moisture sensitivity, and not explosive or expensive. The proposed reaction mechanism for the acetylation of alcohols and phenols using acetic anhydride over ZnCrFeO<sub>4</sub> under solvent free condition at room temperature is shown in the Scheme 2.





**Scheme 2.** The proposed catalytic cycle for the acetylation reaction by  $ZnCrFeO_4$

### Spectral and physical data of some products

**Entry 1 (Table 2).** IR (KBr),  $\nu$  ( $cm^{-1}$ ): 3055 (w), 2915 (w), 1753 (s), 1587 (s), 1485(m), 1364 (s), 1179, 1015 (s), 916 (s), 876, 739, 675; m.p.= 55°C (Reported = 51°C).

**Entry 3 (Table 2).** IR (KBr),  $\nu$  ( $cm^{-1}$ ): 3050 (w), 2955(m), 2925 (w), 1760 (s), 1599 (m), 1464 (m), 1350 (m), 1375 (m), 1222 (m), 1214 (m), 1167 (m); m.p.=70-72°C (Reported = 68–71°C).

**Entry 9. (Table 2).** IR (KBr),  $\nu$  ( $cm^{-1}$ ): 3294 (s), 3261 (w), 3196 (w), 3137(w), 1699 (s), 1536 (m), 1501 (m), 1465 (m), 1393 (m), 1324 (m) 1265 (m), 1180 (m), 1042 (m), 908 (m), 768 (s), 761 (m); m.p.=116-118°C (Reported = 114°C).

**Entry 11. (Table 2).** IR (KBr),  $\nu$  ( $cm^{-1}$ ): 3289 (w), 3088 (w), 2960 (m), 2934 (w), 1655 (s),1558 (s), 1467 (m), 1461 (m), 1453 (m), 1374 (m), 1296 (s), 1228 (m), 1151 (m), 1096 (m), 996 (w), 737 (w); m.p.=119-120 °C (Reported =117°C).

**Entry 12. (Table 2).** IR (KBr),  $\nu$  ( $cm^{-1}$ ): 3291 (m), 2852 (m), 2979 (s), 1614 (s), 1561 (s), 1445 (m), 1374 (s),1363 (m) 1290 (m),1255 (m),1118 (m),1073 (m), 982 (m), 893 (w); m.p.=105-107°C (Reported = 101-103°C).

### Conclusion

In conclusion,  $ZnCrFeO_4$  magnetic nanoparticles is an efficient, ecofriendly, inexpensive, nontoxic, reusable and green catalyst for the acetylation of alcohols, phenols and amines using acetic anhydride. This method is attractive because of its simplicity, clean, efficient, rapid and mild reactions conditions and fast catalyst reusability.

### Acknowledgments

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