# Synthesis, Characterization and Catalytic Application of $V_2O_5/Fe_3O_4$ as Heterogeneous Catalyst for the Synthesis of Quinoline-4-carboxylic Acid Derivatives

## Khillare SL[2], Lande MK[1], Shinde NS[2], Arbad BR[1*]

[1]*Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.), 431004, India*
[2]*Shardabai Pawar Mahila Mahavidyalaya Shardanagar, Malegaon (Bk), Pune (M.S.), 413115, India*

## ABSTRACT

*A series of $V_2O_5/Fe_3O_4$ mixed metal oxides with different wt % of $V_2O_5$ were synthesized by co-precipitation followed by wet impregnation and calcined at 550°C and were characterized by fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), temperature-programmed desorption (NH3-TPD), scanning electron microscope (SEM), Energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) techniques. The prepared materials were tested for catalytic activity by the synthesis of quinoline-4-caboxylic acid derivatives using Doebner reaction (pyruvic acid, aldehydes and amines) in water. The best catalytic activity was obtained with 2.5% $V_2O_5/Fe_3O_4$. This work describes the catalytic behavior of $V_2O_5$ in mixed metal oxide systems.*

**Keywords:** $V_2O_5/Fe_3O_4$, Quinoline-4-caboxylic acid, Doebner reaction

## INTRODUCTION

The use of transition metal oxides mediated reactions in organic synthesis has become of growing importance over the past several decades. In particular, a variety of methods have been developed to carry out various reactions such as redox [1], condensation [2] hydrogenation reaction [3] and several other reactions. Several unique aspects of these metal oxides are responsible for their success: since they have a high adsorption capacity, active sites of different strengths can be generated on the surface. Number of transition metal oxides has been employed for organic transformations in high yield, while maintaining low loadings, high functional group tolerance and mild reaction conditions. Many of these features have been obtained through the proper choice of supporting oxide for the metal catalyst. Traditionally, heterogeneous catalysis is favored than homogeneous catalysis for greater number of applications in both industrial and fundamental research because of its ease of handling, simple experimental conditions, and reusability. In green point of view, there is a constant effort to replace the hazardous catalysts by heterogeneous catalysts, this is due to advantages such as non-toxic nature, inexpensive and easy to reuse. Metal oxides are usually used to synthesize heterogeneous catalysts, though, the separation and recycling of catalysts is complex and not cheap to run. While if the catalyst is magnetic in nature, it can be removed by a magnet [4]. Also there is a growing interest in magnetic ferrite nanoparticles because of their wide applications in permanent magnets, magnetic drug delivery, microwave devices and high density information technology [5-8]. A mixed metal oxide with spinel structure has high chemical and thermal stability, therefore appropriate for ceramics and coloring enamels. Some of the ferrites are also found to be good magnetic, refractory, photoelectric and catalytic activities [9,10].

Quinoline derivatives were broadly studied because of their effective pharmacological and biological activities. Quinoline derivatives are widely used as antagonists [11], antitumour, antiviral and antibacterial activities [12,13] and analgesic agents [14]. Beside this, quinoline-4-carboxylic acid derivatives are the important precursors to synthesize other valuable quinoline derivatives [15]. Therefore, a number of methods have been reported to synthesize quinoline acid derivatives. The synthesis method involve Doebner reaction catalyzed by Ytterbium perfluorooctanoate [16], Skraup [17], Doebner-von Miller [18], Friedlander reaction [19] however, these methods certain drawbacks such as, long reaction time or low yield of products.

Objective of this work is to develop and study of catalytic activity of $V_2O_5$ doped $Fe_3O_4$. Ferrites are magnetic in nature and hence when used as heterogeneous catalyst, it can be separated magnetically. Similarly, it can be used as support for the catalyst such as $V_2O_5$. The magnetic material can be conveniently and efficiently separate from the reaction with an external magnet and then used in another run after washing with *n*-hexane. Thus, bearing in mind the potential catalytic applications of the material, it has been used in various organic transformations for the synthesis of biologically and pharmacologically important compounds. Characterization of $V_2O_5/Fe_3O_4$ was carried out using different modern methods such as FT-IR, XRD, SEM, EDS, TPD and XPS.

**EXPERIMENTAL**

**Materials**

All chemicals used as received and of synthesis grade reagents (Merck).

**Preparation of catalyst**

**Synthesis of $Fe_3O_4$ by co-precipitation method**

In a reaction, calculated amounts of ferrous ammonium sulphate and ferric ammonium sulphate were separately dissolved in deionized water and mixed together drop by drop with continuous stirring. Aqueous ammonia as precipitating agent is used. pH of the solution was adjust to 9 then, the resultant mixture was stirred upto 4 h at 80°C and resultant precipitate was filtered, then washed with water, and dried at 120°C.

**Impregnation of $V_2O_5$ on $Fe_3O_4$**

The $V_2O_5/Fe_3O_4$ materials, containing 2.5 - 10 wt % $V_2O_5$ were prepared by impregnation method. In typical reaction, stoichiometric amount of ferrite is added in the solution of ammonium metavanadate (1 M) and stirred for 4 h and dried. Thus formed powder is calcined at 550°C for 5 h. After calcination $V_2O_5$ doped ferrite is formed.

**General procedure for the quinoline-4-carboxylic acid synthesis**

A mixture of reactants pyruvic acid (10 mmol), amine (11 mmol), and aldehyde (10 mmol) in 20 ml water as solvent was stirred with $V_2O_5/Fe_3O_4$ under reflux conditions for appropriate time (Scheme 1). When the reaction was completed as monitored by TLC, the reaction product was filtered to obtain crude product. This crude residue was added to 10 ml of aq. NaOH (1 M) solution and refluxed for 1 h successively and then the solution was acidified by HCl (1 M). The precipitate was filtered and recrystallized with acetic acid to get pure product. The catalyst remaining was recovered simply by filtration.
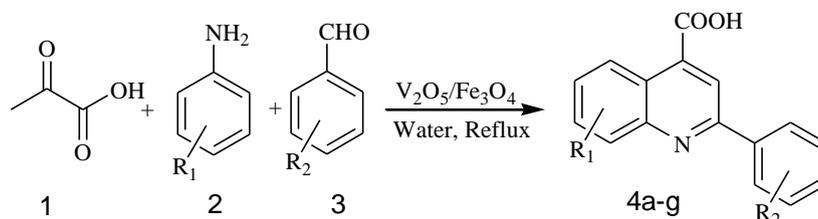


**Scheme 1: Synthesis of quinoline-4-carboxylic acid catalyzed by $V_2O_5/Fe_3O_4$ solid heterogeneous catalyst**

**Spectral data of representative compound**

4c: FTIR (KBr): 3064, 2923, 1708, 753, 694, 509 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO) δ: 7.10 (m) 4H, 7.27 (m) 4H, 8.21 (s) 2H, 11.87 (bs) 1H.
4d: FTIR (KBr): 3292, 1655, 753, 694, 509 cm$^{-1}$; $^1$H NMR (300 MHz, DMSO) δ: 3.24 (s) 3H, 6.82-7.10 (m) 4H, 7.27 (m) 4H, 7.50 2H, 10.05 (bs) 1H.3.

**RESULTS AND DISCUSSION**

**Characterization of $V_2O_5/Fe_3O_4$**

The X-ray diffraction (XRD) patterns of the synthesized $V_2O_5/Fe_3O_4$ were recorded on a Bruker D8 advance X-ray diffractometer using Cu Kα radiation with a wavelength of 0.154056 nm. For the study of surface morphology of scanning electron microscopy (SEM) analyses were carried out with a JEOL JSM-6330 LA operated at 20.0 kV and 1.0 nA. The elemental composition was examined using an energy dispersive spectrophotometer (EDS). temperature programmed desorption of ammonia (NH$_3$-TPD) measurements were carried out on a Micromeritics Chemisoft TPx V1.02 and X-ray photoelectron spectroscopy (XPS, ESCA-3000-VG Microtech, Uckfield, UK) was used to study the chemical composition.

**XRD analysis**

The X-ray diffraction pattern of catalyst $V_2O_5/Fe_3O_4$ calcined at 550°C is shown in Figure 1. In XRD pattern, it is observed that there are small differences between the relative intensities and width of reflexes, which shows the differences in crystallite size. The XRD pattern of the $Fe_3O_4$ sample is shown in Figure 1a. The distinct peaks can be indexed at 2θ=29.916, 35.235, 42.817, 54.294, 63.231 and 75.491 from the reflection indexed as (220), (311), (400), (430), (441) and (542) planes of a cubic unit cell, which corresponds to that of magnetite structure (JCPDS card no. 79-0418), the sample show broad peaks, indicating the ultra-fine nature and small crystallite size of the particles.

Figure 1b-1e) shows the XRD patterns of different wt% $V_2O_5/Fe_3O_4$ prepared with the wet impregnation method. The XRD pattern of 2.5% $V_2O_5/Fe_3O_4$ did not contain any Vanadia peak Figure 1b which indicates that the Vanadia was well dispersed on the ferrite surface, which shows that there is no well-defined crystalline phase of vanadium oxide in 2.5% $V_2O_5/Fe_3O_4$ catalysts, however, for 5% $V_2O_5/Fe_3O_4$ and 7.5% $V_2O_5/Fe_3O_4$ peaks at 2θ=25.83 from the reflection of plane (110) from crystalline $V_2O_5$, though very weak, but can be observed Figure 1(c-d). The peaks corresponding to crystalline $V_2O_5$ are very sharp for 10% $V_2O_5/Fe_3O_4$ Figure 1e. From this analysis, it could be concluded that crystalline $V_2O_5$ is well dispersed on surface of ferrite at lower wt% but as its percentage, increases the hexagonal cubic phase of Vanadia is formed [20].
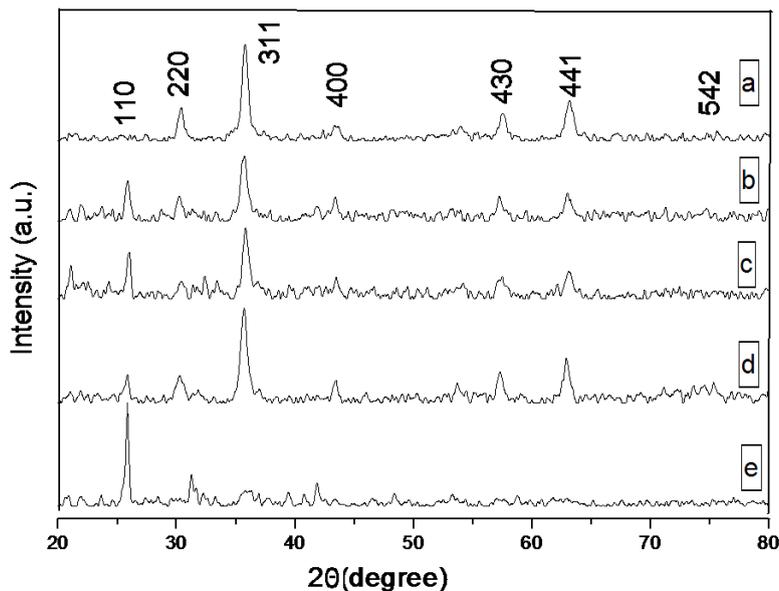
**Figure 1: XRD pattern of series of (a) Fe$_3$O$_4$, (b) 2.5%, (c) 5%, (d) 7.5% and (e) 10% V$_2$O$_5$/Fe$_3$O$_4$ calcined at 550°C**

The values of lattice parameter 'a' for the prepared sample are in good agreement to the reported values in some references [21,22]. The crystallite size of the particles were calculated using the full width at half maximum (FWHM) values of (311) reflection of the X-ray diffraction by Scherrer's equation. The calculated values of average crystallite size and lattice parameter of the samples are listed in Table 1.

**Table 1: XRD analysis of V$_2$O$_5$/Fe$_3$O$_4$ samples**

| Sample | Crystallite size (nm) | Lattice constant A° |
|---|---|---|
| Fe$_3$O$_4$ | 138.908 nm | 8.324 |
| 2.5% V$_2$O$_5$/Fe$_3$O$_4$ | 130.59 nm | 8.324 |
| 5% V$_2$O$_5$/Fe$_3$O$_4$ | 125.14 nm | 8.324 |
| 7.5% V$_2$O$_5$/Fe$_3$O$_4$ | 71.344 nm | 8.324 |
| 10% V$_2$O$_5$/Fe$_3$O$_4$ | 70.9138 nm | 8.324 |

**FT-IR analysis**

The FT –IR spectra of synthesized V$_2$O$_5$/Fe$_3$O$_4$ using dry KBr as a standard reference in the range of 4000-500 cm$^{-1}$ are shown in Figure 2. IR spectra shows that in each sample (a-e) there is a broad peak in the range 3500-3200 cm$^{-1}$ due to hydroxyl group which is adsorbed on the surface of the ferrite, similarly the peak in the range 1600-1500 and 1450-1400 cm$^{-1}$ in all samples is due to the deformation of the surface hydroxyl groups [23]. Two main metal-oxygen bands are seen in the range 1000-400 cm$^{-1}$, in all samples. In all spinels and mostly in ferrites, two main broad metal oxygen bands are seen in FT-IR spectra, the higher band observed at 600 cm$^{-1}$, due to intrinsic stretching vibrations of metal-oxygen bond at tetrahedral site, (M$_{tetra}$-O), while the lower band, that observed at 500 cm$^{-1}$ is assigned to octahedral metal stretching vibration (M$_{octa}$-O) [24]. This is confirmed from Fourier Transform Infrared Spectroscopy (FT-IR) that the structure remains cubic spinel after impregnation of V$_2$O$_5$ in Fe$_3$O$_4$ [25].
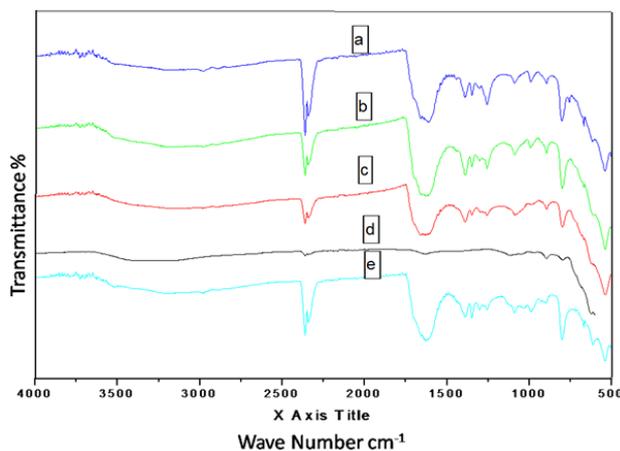


**Figure 2: FT-IR spectra of series of (a) Fe$_3$O$_4$, (b) 2.5%, (c) 5%, (d) 7.5% and (e) 10% V$_2$O$_5$/Fe$_3$O$_4$ calcined at 550°C**

**SEM and EDS analysis**

The surface morphology of $V_2O_5/Fe_3O_4$ samples is studied by scanning electron micrograph shown in Figure 3. The SEM micrograph of $V_2O_5/Fe_3O_4$ catalyst shows particles are homogeneously aggregated and have irregular shapes. The surface morphology of the catalyst as seen from the SEM consists of the grains, with relatively homogeneous grain distribution, with an average grain size varying from 1.0 to 5.0 μm.
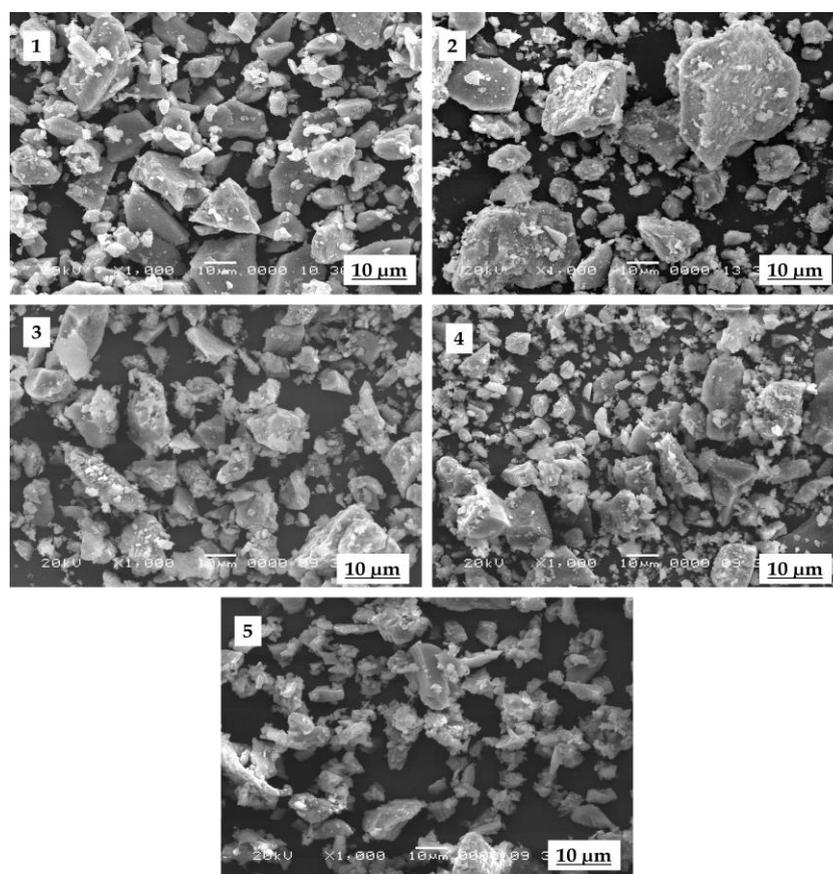
**Figure 3: SEM images of series of (a) Fe₃O₄, (b) 2.5%, (c) 5%, (d) 7.5% and (e) 10% V₂O₅/Fe₃O₄ calcined at 550°C**

Energy dispersive X-ray spectroscopy (EDS) is a technique used for elemental analysis. The EDS patterns which are obtained for all the samples give the elemental composition which is shown in Table 2. The EDS pattern shows the presence of V, Fe and O elements.

**Table 2: Elemental composition of V₂O₅/Fe₃O₄ Samples**

| Catalyst | Mass % | | | Total |
|---|---|---|---|---|
| | V | Fe | O | |
| Fe₃O₄. | 0 | 72.36 | 27.64 | 100 |
| 2.5% V₂O₅/Fe₃O₄ | 1.1 | 70.93 | 27.97 | 100 |
| 5% V₂O₅/Fe₃O₄ | 2.23 | 69.48 | 28.29 | 100 |
| 7.5% V₂O₅/Fe₃O₄ | 3.36 | 68.02 | 28.62 | 100 |
| 10% V₂O₅/Fe₃O₄ | 4.51 | 66.54 | 28.95 | 100 |

**NH₃-TPD analysis**

NH₃-TPD measurements were studied by i) Preheating the 297 mg ferrite sample to 500°C with 20°C/min in helium with flow rate 30 ml/min; ii) Adsorption of NH₃ at room temperature; iii) Desorption of adsorbed NH₃ with heating rate 20°C/min from room temperature to 550°C. The total acidity of sample was detected by temperature programme desorption of ammonia. Total acidity of 2.5% V₂O₅/Fe₃O₄ is 0.54417 mmol/g. NH₃-TPD curve shown in Figure 4.
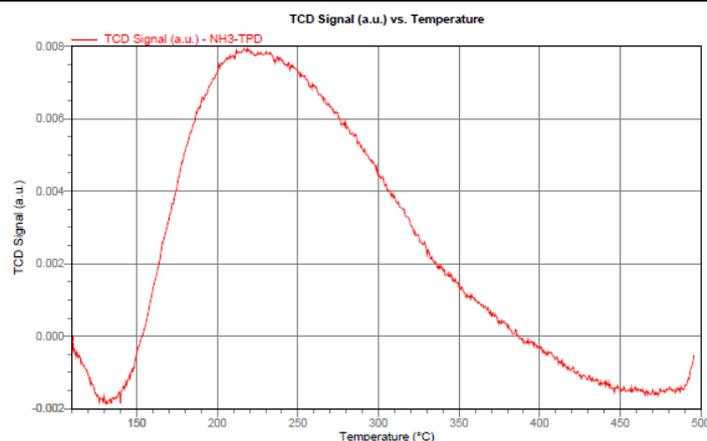
**Figure 4: NH$_3$-TPD curve for TCD signal (a. u.) vs. Temperature (°C) of the sample 2.5% V$_2$O$_5$/Fe$_3$O$_4$ calcined at 550°C**

### X-ray photoelectron spectroscopy

The powder XPS pattern of V$_2$O$_5$/Fe$_3$O$_4$ catalyst is shown in Figure 5. The chemical state of the elements was determined by calculating the binding energy with reference to C1s peak at 284.9 eV. From the Figure 5 it is observed that the Fe 2p1/2 and 2p3/2 peaks situated at around 711 and 724 eV are broadened due to the existence of the both Fe$^{2+}$ and Fe$^{3+}$ ions. The measured Fe 2p3/2 (Fe 2p1/2) binding energy is 709.7 (722.7 eV) for Fe$^{2+}$ and 711.15 eV (724.25 eV) for Fe$^{3+}$. These values match very well to the literature values [26]. Thus, the XPS study revealed the presence of Fe$_3$O$_4$. The binding energies of the V 2p levels are 516.9 and 524.25 eV for V 2p3/2 and V 2p1/2, respectively, Which suggests pentavalent oxidation state of vanadium, these are slightly lower than the literature values for stoichiometric V$_2$O$_5$ [27]. However, that observed for V$_2$O$_5$ suggests lower electron density, i.e., higher acidity of catalyst [28].
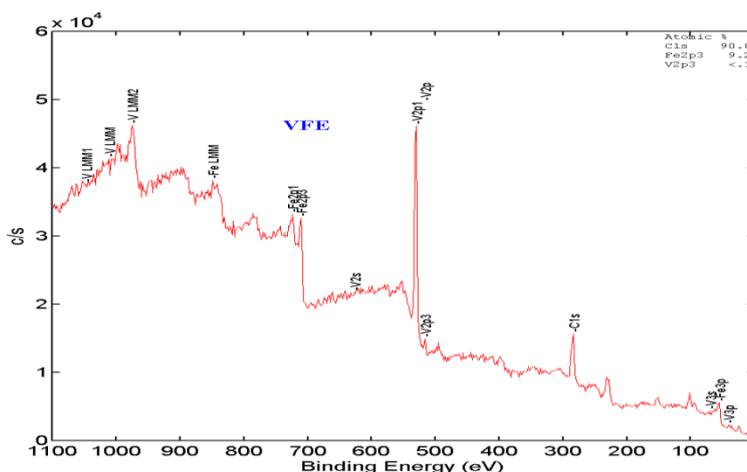


**Figure 5: High resolution XPS spectra of 2.5% V$_2$O$_5$/Fe$_3$O$_4$**

### Catalytic activity results

One pot four component reactions of aldehydes, pyruvic acid and amines to provide quinoline-4-carboxylic acid derivatives catalyzed by V$_2$O$_5$/Fe$_3$O$_4$, is shown in Scheme 1.

In order to study catalytic activity of different wt% of V$_2$O$_5$ in V$_2$O$_5$/Fe$_3$O$_4$ as catalyst, the reaction of pyruvic acid, amine and aldehyde was carried out using the different wt% of V$_2$O$_5$ (Table 3). It is observed that, 2.5 wt% of V$_2$O$_5$ in V$_2$O$_5$/Fe$_3$O$_4$ have better catalytic activity.

**Table 3: Synthesis quinoline-4-carboxylic acid derivatives using different wt% of V$_2$O$_5$ in V$_2$O$_5$/Fe$_3$O$_4$ as catalyst**

| Entry | wt% of V$_2$O$_5$ in V$_2$O$_5$/Fe$_3$O$_4$ | Time (min) | Isolated yield[b] % |
|-------|---------------------------------------------|------------|---------------------|
| 1 | Nil | 120 | 44 |
| 2 | 2.5 | 120 | 94 |
| 3 | 5 | 120 | 57 |
| 4 | 7.5 | 120 | 50 |
| 5 | 10 | 120 | 35 |

[a]Reaction conditions pyruvic acid (10 mmol); amine (11 mmol) and aldehyde (10 mmol) in 20 ml of water and V$_2$O$_5$/Fe$_3$O$_4$ 0.2 g refluxed; [b]Isolated yield

Our initial work was focused on the optimization of the amount of V$_2$O$_5$/Fe$_3$O$_4$ by using pyruvic acid (10 mmol), amine (11 mmol) and aldehyde (10 mmol) in 20 ml of water and variable amount of V$_2$O$_5$/Fe$_3$O$_4$ (Table 4). It was observed that 0.2 g V$_2$O$_5$/Fe$_3$O$_4$ effectively catalyzed the reaction with good yield. Higher amount of catalyst did not show major effect on the reaction time. The reaction was also investigated using Fe$_3$O$_4$ however with poor yield.

**Table 4: Optimization the amount of V$_2$O$_5$/Fe$_3$O$_4$ for quinoline-4-carboxylic acid synthesis**

| Entry | Catalyst (g) | Time (min) | Yield (%)[b] |
|-------|--------------|------------|--------------|
| 1 | Without catalyst | 120 | No reaction |
| 2 | 0.1 | 120 | 66 |
| 3 | 0.2 | 120 | 94 |
| 4 | 0.3 | 120 | 94 |

[a]Reaction conditions: pyruvic acid (10 mmol); amine (11 mmol) and aldehyde (10 mmol) in 20 ml of water and V$_2$O$_5$/Fe$_3$O$_4$ refluxed; [b]Isolated yield

The V$_2$O$_5$/Fe$_3$O$_4$ was regenerated by filtration and reused after washing with *n*-hexane and dried at 60°C and activated at 120°C for 1 h and retained the same catalytic activity. The reusability of the catalyst was studied for the aniline and acetic acid. The regenerated catalyst showed similar catalytic activity till 4th reaction cycle with almost consistent activity (Table 5).

**Table 5: Reusability of V$_2$O$_5$/Fe$_3$O$_4$ for synthesis of quinoline-4-carboxylic acid derivatives[a]**

| Entry | Cycle | Yield (%)[b] |
|-------|-------|--------------|
| 1 | Fresh | 94 |
| 2 | 1st | 94 |
| 3 | 2nd | 92 |
| 4 | 3[td] | 90 |
| 5 | 4th | 90 |

[a]Reaction conditions pyruvic acid (10 mmol); amine (11 mmol) and aldehyde (10 mmol) in 20 ml of water and V$_2$O$_5$/Fe$_3$O$_4$ 0.2 g refluxed; [b]Isolated yield

After determining the optimum amount of catalyst, in similar manner numbers of substituted aldehydes are used for synthesis of quinoline-4-carboxylic acid derivatives in presence of catalytic amount of V$_2$O$_5$/Fe$_3$O$_4$ (0.2 g) at reflux temperature with good yields (Table 6). All the reactions for different derivatives were carried out neatly and easily in presence of V$_2$O$_5$/Fe$_3$O$_4$ to produce quinoline-4-carboxylic acid derivatives in excellent yields and no undesirable by-products are observed. The experimental work up is very simple and has an ability to tolerate a variety of other functional groups such as NO$_2$, Me, Cl, OMe, and OH. It was indicated that electron rich aldehydes shows higher yield than electron deficient aldehydes.

**Table 6: Synthesis of quinoline-4-carboxylic acid derivatives catalyzed by V$_2$O$_5$/Fe$_3$O$_4$[a]**

| Entry | R$_1$ | R$_2$ | Time (min.) | Yields (%)[b] | M.P. (°C) Observed | M.P. (°C) Literature |
|-------|-------|-------|-------------|---------------|----------|------------|
| 4a | H | H | 120 | 94 | 211-213 | 210-215 [29] |
| 4b | H | 4-NO$_2$ | 120 | 91 | 270-272 | 271-273 [16] |
| 4c | H | 4-Cl | 120 | 89 | 233-235 | 230-232 [16] |
| 4d | H | 4-OCH$_3$ | 120 | 93 | 214-216 | 216-217 [16] |
| 4e | 4-CH$_3$ | 4-CH$_3$ | 120 | 94 | 241-243 | 238-246 [16] |
| 4f | 4-CH$_3$ | 4-NO$_2$ | 120 | 85 | 260-262 | 265-266 [16] |
| 4g | 4-CH$_3$ | H | 120 | 88 | 216-218 | 218-219 [16] |

[a]Reaction conditions pyruvic acid (10 mmol); amine (11 mmol) and aldehyde (10 mmol) in 20 ml of water and V$_2$O$_5$/Fe$_3$O$_4$ 0.2 g refluxed; [b]Isolated yield

## CONCLUSION

In conclusion, the Doebner reaction in water was firstly reported by using V$_2$O$_5$/Fe$_3$O$_4$ as a catalyst to synthesize quinoline-4-carboxylic acids in good yields. The method has many advantages such as, recyclability of the catalyst, short reaction time, high atom economy, small amount of catalyst and especially the avoidance of harmful organic solvents, which provide a green and efficient method for Doebner reaction.

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