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$ZnAl_2O_4$@ZnO AN EFFECTIVE, HETEROGENEOUS CATALYST FOR THE SYNTHESIS OF *β*-ENAMINONES AND *β*-ENAMINOESTERS

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Abstract. Using $ZnAl_2O_4$@ZnO as a catalyst, an environmentally friendly and very effective method has been developed to selectively add a ring to 1,3-dicarbonyl compounds and aromatic, aliphatic primary amines. A wide variety of bis(*β*-enaminones) and bis(*β*-enaminoesters) can be synthesized using this highly versatile method, which provides good yields. This procedure can be carried out at room temperature, which is environmentally advantageous as it utilizes $ZnAl_2O_4$@ZnO as a heterogeneous, recyclable and stable catalyst under free solvent conditions. A co-precipitation reaction at constant pH was used to prepare this catalyst, and spectral analysis (X-ray diffraction, FTIR) and morphological characterization techniques (SEM, EDX) confirmed its morphological structure.

Keywords: bis(*β*-enaminoester), bis(*β*-enaminone), free solvent condition, condensation, heterogeneous catalyst.

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Introduction

β-Enaminones and *β*-enaminoesters play a pivotal role as essential intermediates in organic synthesis due to their dual nature as electrophiles and nucleophiles [1]. These compounds are incredibly useful for the preparation of a wide range of important bioactive heterocyclic compounds and various biologically active substances [2]. Due to their wide range of pharmaceutical activities and their importance as key intermediates in organic synthesis, organic chemists place great emphasis on the synthesis of these compounds [3].

A typical process for the preparation of *β*-enaminones and *β*-enaminoesters is the direct condensation of a *β*-dicarbonyl with amines at reflux in an aromatic solvent after azeotropic elimination of water [4]. Different types of catalysts such as metal nanoparticles [5], metal triflate [6], phosphoric anhydride/MW [7], metal oxide [8], BF_3–OEt_2 [9], $AlPO_4$ [10], $Ca(CF_3COO)_2$ [11], Moroccan rock phosphate [12], Nb_2O_5/g-C_3N_4 [13], onion extract [14], Mesh silica gel [15], KH_2PO_4 [16], Amberlyst-15 [17], melamine-formaldehyde resin supported [18], $BiCl_3$ [19], P_2O_5/SiO_2 [20], $Zn(OAc)_2$ [21], and water [22] are usually used. However, some of these methods present synthesis challenges. For example, they require expensive catalysts, toxic solvents, and metal catalysts. The reactions are also time-consuming and require large amounts of catalyst. In addition, yields are low, preparation steps are long and tedious, and chemoregional selectivity is absent.

The $ZnAl_2O_4$@ZnO catalyst, prepared by heating the [Zn-Al-Cl] phase to a constant 900°C, is stable at both high and low temperatures [23]. Moreover, a wide range of catalytic reactions, including cracking, dehydrogenation, hydrogenation, dehydrogenation, and pollution control, employ $ZnAl_2O_4$@ZnO [24-26].

This study aims to develop a promising method by establishing a novel, clear, and rapid technique for the synthesis of *β*-enaminoesters and *β*-enaminones. The flexibility of this method allows for the synthesis of a diverse range of bis(*β*-enaminones) and bis(*β*-enaminoesters) at room temperature. This is beneficial for the environment since it utilizes $ZnAl_2O_4$@ZnO as a heterogeneous catalyst, which is both recyclable and stable under free solvent conditions. This research focuses on improving the condensation processes between 1,3-dicarbonyl compounds and primary amines. This is achieved by using $ZnAl_2O_4@ZnO$, a nanocatalyst that is both inexpensive and environmentally friendly. The application of this approach not only facilitates comprehension of the synthesis process, but also offers an environmentally sustainable and economically viable alternative in the field of organic chemistry.

Experimental

Materials

Analytical grade chemicals including $ZnCl_2·6H_2O$, $AlCl_3·6H_2O$, sodium hydroxide (NaOH), ethyl acetoacetate, acethylacetone, and all primary amines were purchased from Janssen Chemica, Loba Chimie, and Sigma-Aldrich.

Instruments

The *^1H and ^{13}C NMR spectra* were recorded on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz, respectively, in $CDCl_3$ solvent.

Morphological characterization was conducted using a HIROX SH4000M scanning electron microscope (SEM) operating at 5kV to 30kV variable acceleration voltage, equipped with an energy dispersive X-ray (EDX) detector for chemical composition analysis.

X-ray diffraction (XRD) measurements were also carried out and XRD diagrams were collected in the θ–θ mode using a Philips X'Pert MPD diffractometer using Cu K_α radiation (λ= 1.54178 Å) at room temperature (25°C); 2θ= 4–80.

Fourier-transform infrared (FTIR) *spectra* were obtained utilizing a Nicolet is 5 Thermo scientific spectrometer. Pellets were composed of 100 mg of finely powdered KBr and 2 mg of the sample.

Melting point values (m.p.) were determined on Kofler Banc apparatus.

Preparation of $ZnAl_2O_4@ZnO$ catalyst

The [Zn–Al–Cl] precursor was prepared by a co-precipitation method at constant pH. A homogeneous mixture of $ZnCl_2$ and $AlCl_3$ aqueous solutions with a molar ratio of $[Zn^{2+}]/[Al^{3+}]$= 2 was slowly added under stirring to a reactor containing 250 mL of freshly deionized water. The pH of the solution was kept constant at 9 by adding 1.0 M NaOH solution. The resulting precipitate was filtered, repeatedly washed with water, and dried at room temperature [27]. To avoid or reduce contamination by atmospheric CO_2, all experiments were performed under a stream of N_2. The resulting matrix was calcined for 6 h in an oven maintained at 900°C.

General procedure for the synthesis of bis(β-enaminones) and bis(β-enaminoesters)

In a typical experiment, a mixture of *β*-dicarbonyl (1.7 mmol), primary amine (1.7 mmol) and $ZnAl_2O_4@ZnO$ (15 mg) was stirred at room temperature for appropriate time. At the end of the reaction, 10 mL of distilled water was added to the residue and extracted with diethyl ether (3×25 mL). The organic layer was thoroughly dried using Na_2SO_4. After evaporating the solvent under reduced pressure, pure bis(*β*-enaminones) and bis(*β*-enaminoesters) are successfully isolated through column chromatography over silica gel, using a mixture of hexane and ethyl acetate as the eluent (95/5). All isolated pure products were thoroughly characterized using ^1H, ^{13}C NMR and mass spectra, or otherwise compared with the known compounds.

Spectral data for selected products

Ethyl-(Z)-3-(2-methyl, 4-chloro-anilinlamino)but-2-enoate (entry 13, Table 1), m.p. 148–150°C, ^1H NMR: δ 1.49 (t, *J*= 6.9 Hz, 3H), 2.04 (s, 3H), 2.46 (s, 3H), 4.34 (q, *J*= 6.9 Hz, 2H), 4.93 (s, 1H), 7.18-7.41 (m, 3H, Ar), 10.31 (br s, 1H, NH); ^{13}C NMR, δ: 14.65, 18.03, 20.05, 58.84, 86.84, 126.19, 127.13, 130.31, 130.85, 135.40, 136.45, 159.01, 170.61.

(2Z,2Z')-Diethyl 3,3'-[butane-1,4-diylbis (azanediyl)]bis(but-2-enone) (entry 15, Table 1), m.p. 110–112°C, ^1H NMR: δ 1.11 (t, *J*= 6.9 Hz, 3H), 1.56 (s, 2H), 1.81 (s, 3H), 3.14 (d, *J*= 5.7 Hz, 2H), 3.98 (q, *J*= 6.9 Hz, 2H), 4.87 (s, 1H), 10.80 (br s, 1H, NH); ^{13}C NMR: δ 18.65, 22.93, 26.76, 28.59, 38.59, 42.42, 95.83, 162.51, 170.05, 194.31.

(2Z,2Z')-Diethyl 3,3'-[hexane-1,6-diylbis (azanediyl)]bis(but-2-enone) (entry 16, Table 1), m.p. 115–117°C, ^1H NMR: δ 1.21 (t, *J*= 6.9 Hz, 3H), 1.56 (m, 4H), 1.81 (s, 3H), 3.16 (m, 2H), 4.02 (q, *J*= 6.9 Hz, 2H), 4.42 (s, 1H), 8.56 (br s, 1H, NH); ^{13}C NMR: δ 14.55, 26.66, 30.17, 42.72, 58.05, 81.84, 161.73, 170.50.

(2Z,2Z')-Diethyl 3,3'-[hexane-1,6-diylbis (azanediyl)]bis(but-2-enoate) (entry19, Table 1), m.p. 105–107°C, ^1H NMR: δ 1.21 (t, *J*= 6.9 Hz, 3H), 1.56 (m, 4H), 1.81 (s, 3H), 3.16 (m, 2H), 4.02 (q, *J*= 6.9 Hz, 2H), 4.42 (s, 1H), 8.56 (br s, 1H, NH); ^{13}C NMR: δ 14.55, 19.20, 26.66, 30.17, 42.72, 58.05, 81.84, 161.73, 170.50.

Results and discussion

Characterization of catalyst

The calcination of hydrotalcites leads to their dehydration, followed by de-hydroxylation and collapse of the lamellar structure. Figure 1 shows the XRD pattern for $ZnAl_2O_4@ZnO$.

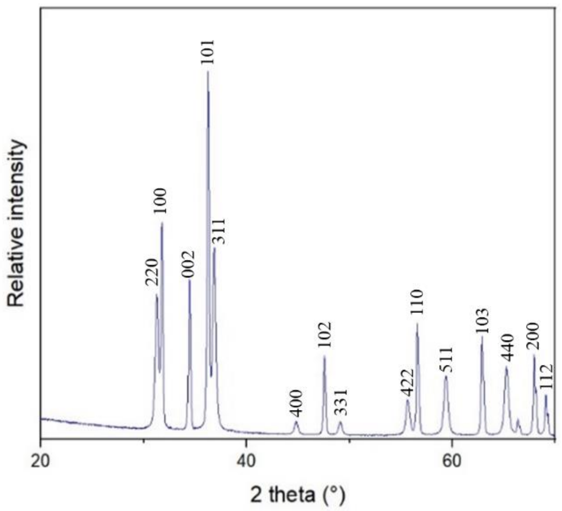


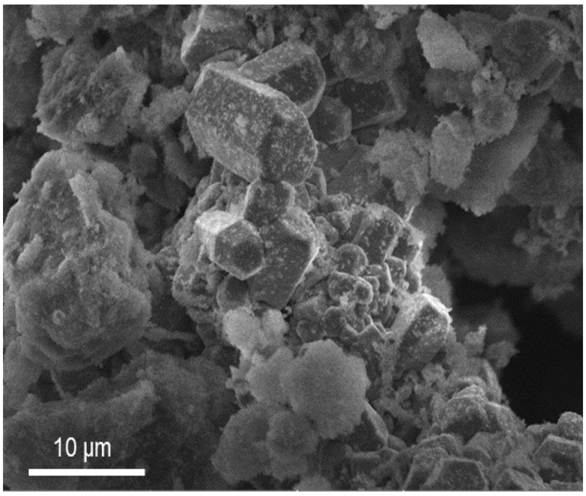
Figure 1. X-ray diffraction patterns of the [Zn-Al-Cl] phase calcined at 900°C.

All diffraction peaks can be perfectly indexed to face-centred cubic spinel-structured $ZnAl_2O_4$ [23]. The characteristic peaks at 2θ of 31.2°, 31.8°, 34.51°, 36.37°, 36.75°, 44.7°, 47.65°, 49.1°, 56.71°, 59.3°, 62.97°, 65.3°, and 68.07° correspond to (220), (100), (220), (002), (101), (400), (102), (110), (331), (511), (103), (440), and (120).

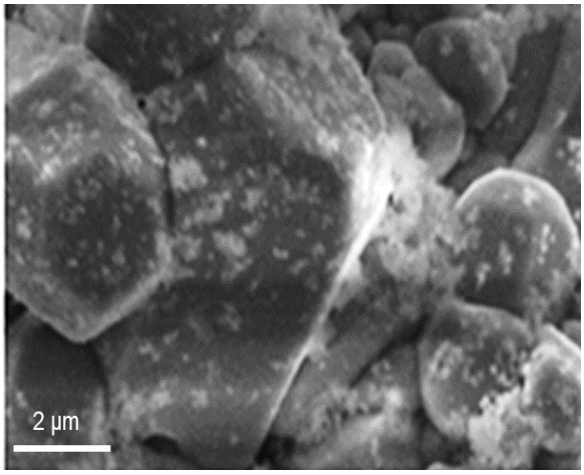
Figure 2 shows the SEM images of the $ZnAl_2O_4$@ZnO calcined at 900°C. Figure 2*(a)* reveals the morphology of $ZnAl_2O_4$@ZnO, which exhibits agglomeration and a slightly irregular contour. Both the large particles, which have a volume of 6×4×4 μm, and the small particles, which have a volume of 3×1×1 μm, have maintained a nearly identical size. The smallest particles harmoniously scatter among the larger ones. These results are in agreement with the sharpness of the peaks observed in the X-ray diffraction patterns.

An EDX spectrum of [Zn-Al-Cl] matrix calcined at 900°C suggesting, for example, 19.87% by weight O, 60.72% by weight Zn, and 19.41% by weight Al (when the totals are normalized to 100) will be labelled. They indicate the disappearance of peaks related to chloride ions. This result is in agreement with the formation of ZnO oxide and $ZnAl_2O_4$ spinel phase.

After calcination of the samples at 900°C (Figure 3), a weakening of the intensity of the vibrations' bands characterizing O–H and C–O groups is observed. In the region below 800 cm^{-1}, there are bands associated, according to the literature, with the vibrational mode of the M–O bond where M represents the elements Zn or Al [28].



(a)



(b)

Figure. 2. SEM micrographs of the [Zn-Al-Cl] calcined at 900°C at two different scales.

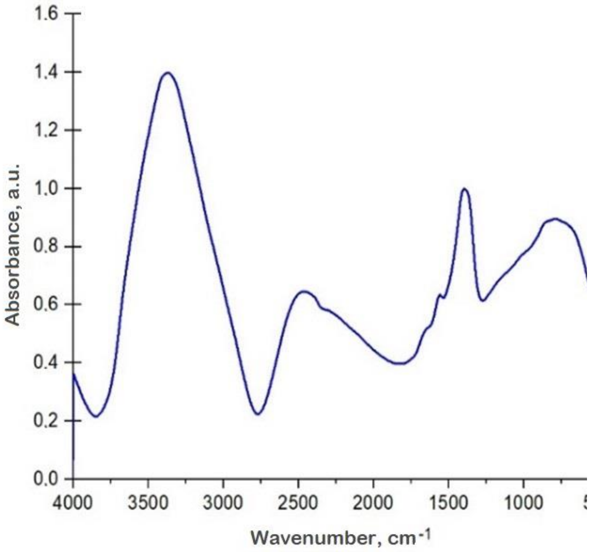


Figure 3. FTIR spectrum of the [Zn-Al-Cl] phase calcined at 900°C.

Catalyst application

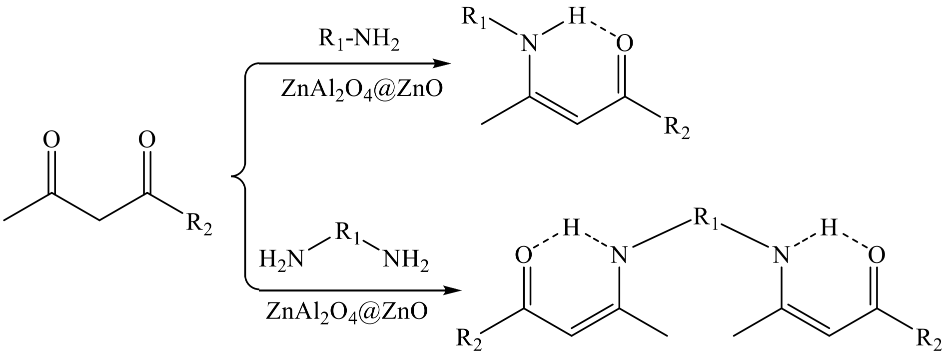
The reaction between aniline and ethyl acetoacetate is conducted as a model reaction at room temperature under free solvent conditions and 15 mg of $ZnAl_2O_4$@ZnO. After stirring, the reaction mixture for 40 minutes gives 3-(phenylamino)-pent-2-enone with a 90% yield (entry 1, Table 1). The modelled reaction was performed without catalysing. Only 30% of the product was obtained, even after stirring for 24 hours (entry 2, Table 1). An increase in the amount catalytic of $ZnAl_2O_4$@ZnO above 15 mg did not significantly improve the yield, while a reduction in the amount of $ZnAl_2O_4$@ZnO to 5 mg reduced the yield (entry 3, Table 1). Obtaining lower yields of the desired product was a common outcome when using solvents like ethanol, ethyl acetoacetate, dichloromethane, and acetonitrile. Similarly, longer reaction times exhibited the same pattern. Under the same operating conditions, the condensation of secondary amines such as piperidine with ethyl acetoacetate does not yield the desired products.

The reaction was conducted in the absence of solvent. After determining the optimal experimental conditions, the range of the reaction was investigated, with some representative results summarized in Table 1. By examining a wide range of substrates, the current methodology displayed remarkable efficiency, as shown in Table 1, indicating its broad applicability. Typically, primary amines and diamines can react with a variety of 1,3-dicarbonyl compounds to produce β-enaminones, β-enaminoesters, bis(β-enaminones), and bis(β-enaminoesters) with excellent yields and in a relatively short time (Scheme 1).

Some aromatic amines that have electron withdrawing groups, like nitro and chloro groups, showed a strong deactivating effect. As a result, the conversion of these amines into the corresponding products had a lower yield (see entries 5 and 10, Table 1). On the other hand, aromatic amines with electron-donating substituents showed higher reactivity and resulted in improved yields of the respective product (see entries 2, 3, 6, Table 1).

Conversely, different diamines such as 1,2-diaminopropane, 1,4-diaminobutane, and 1,6-diaminohexane were combined with various β-dicarbonyl substances like pentane-2,4-dione and ethyl 3-oxobutanoate. The results indicate that $ZnAl_2O_4$@ZnO effectively catalyses the condensation reaction between β-dicarbonyl compounds and diamines, offering an exceptionally fast and practical alternative pathway for the synthesis of potentially bis(aminoenone) compounds. Overall, β-ketoesters are more reactive than β-diketones. In β-ketoesters, the ester group is less reactive than the ketone group. Different 1,3-dicarbonyl compounds, such as pentane-2,4-dione or ethyl 3-oxobutanoate, were condensed with a range of diamines, including aliphatic diamines. Table 1 provides a summary of the findings.

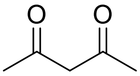
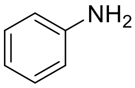
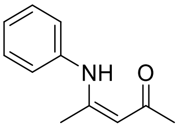
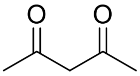
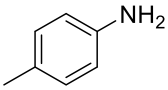
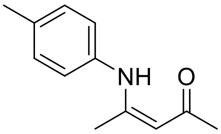
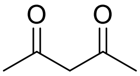
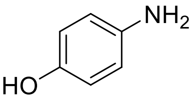
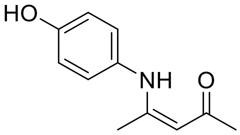
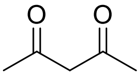
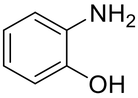
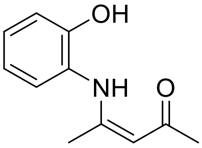
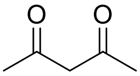
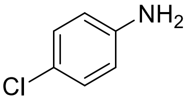
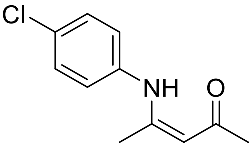
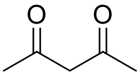
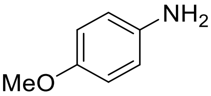
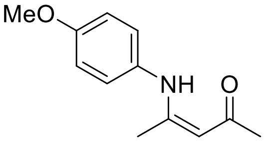
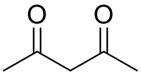
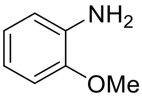
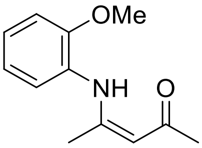
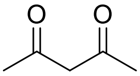
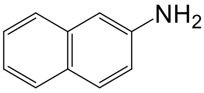
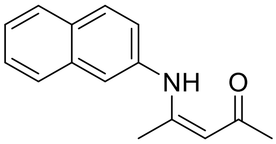
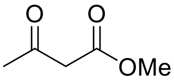
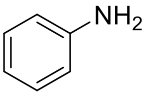
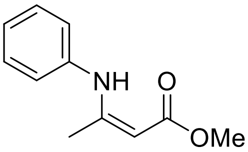
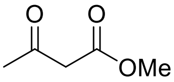
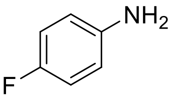
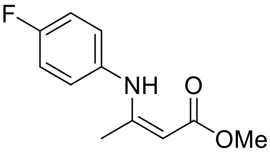
The use of $ZnAl_2O_4$@ZnO provides a highly efficient and economically viable alternative route for synthesizing potential bis(β-enaminones) and bis(β-enaminoesters) compounds. β-Ketoesters exhibit higher reactivity compared to β-diketones in all reactions. When it comes to β-ketoesters, the ketone groups exhibit higher reactivity compared to the ester group. There could be multiple products formed in this reaction. For instance, the amine has the potential to react with either one or both of the carbonyl groups. This is because the starting material contains two carbonyl groups, and two equivalents of amine have been added. It is interesting to note that despite the expected formation of three products from the β-ketoester and two products from the 1,3-diketone, only enaminones were observed as the resulting products.



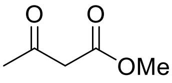
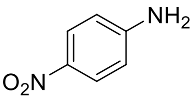
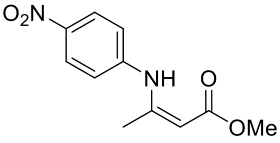
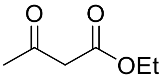
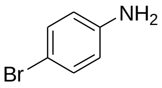
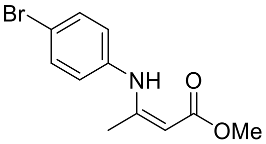
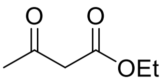
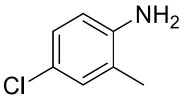
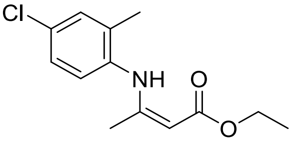
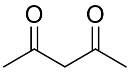
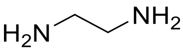
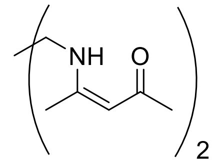
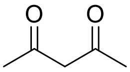
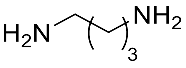
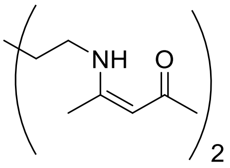
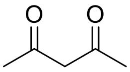
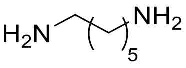
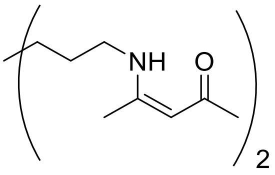
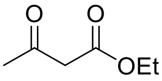
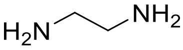
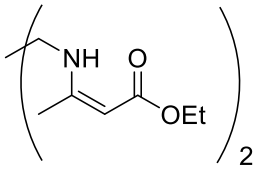
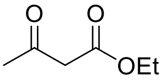
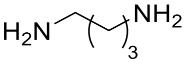
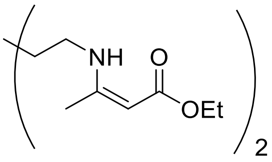
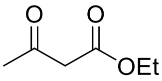
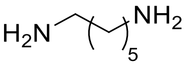
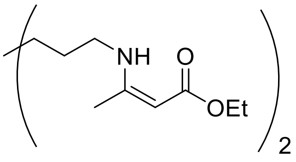
Scheme 1. The general scheme for synthesis of β-enaminones, β-enaminoesters, bis(β-enaminones) and bis(β-enaminoesters).

Table 1

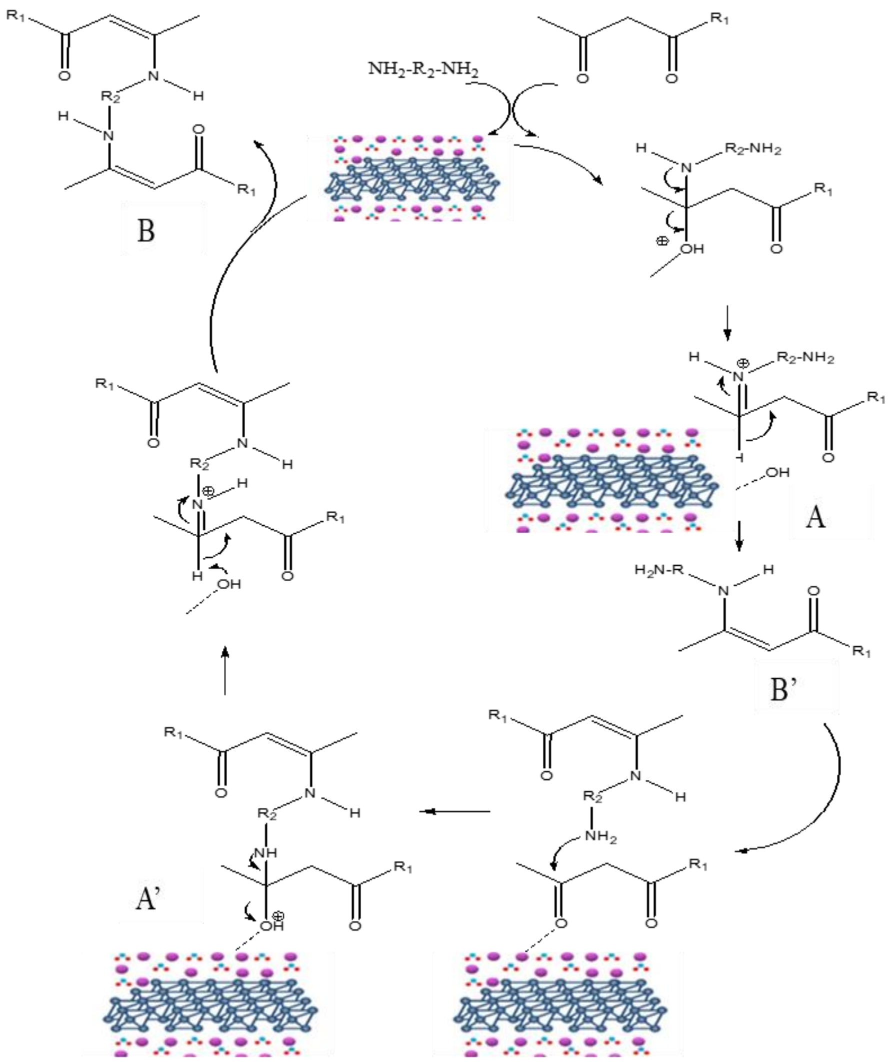
Condensation of *β*-ketones, *β*-ketoesters compounds with various amines, diamines in the presence of $ZnAl_2O_4$@ZnO.

Entry	*β-dicarbonyl*	*Primary Amine*	*Product*	*Time(min)*	*Yield(%)^a*	*References*
1				40 24h	90 30^a	[11]
2				25	96	[11]
3				25	78	[10]
4				25	70	[10]
5				30	84	[11]
6				25	92	[11]
7				120	60	[11]
8				120	80	[31]
9				120	92	[10]
10				100	76	[11]

Continuation of Table 1

Entry	*β-dicarbonyl*	*Primary Amine*	*Product*	*Time(min)*	*Yield(%)*[a]	*References*
11				120	42	[10]
12				45	86	[10]
13				120	65	Current study
14				15	72 [b]	[16]
15				15	80 [b]	Current study
16				15	78[b]	Current study
17				25	96 [b]	[16]
18				25	94 [b]	[29]
19				25	98 [b]	Current study

[a]Isolated yield; [b]2 equiv of ethyl 3-oxobutanoate or pentane-2,4-dione with 1 equiv of diamine.



Scheme 2. Proposed mechanism for $ZnAl_2O_4@ZnO$ catalysed formation of bis(*β*-enaminones) and bis(*β*-enaminoesters).

In the ^{1}H NMR spectra of enaminoesters (entries 17–19, Table 1), there is a noticeable broad singlet in the 8.5–8.6 ppm region, indicating the presence of the NH group in its enaminoester form. However, for enamino ketones (entries 14–16, Table 1), the signal was shifted to 10.8–10.87 ppm, indicating an intramolecular hydrogen bond between the NH group and the ketone group [10-12,29-31]. However, experimental data revealed the presence of enaminoketones and enaminoesters, most commonly in the form of enamine. The parent keto forms were not detected.

In Scheme 2, an attempt is made to illustrate the proposed mechanism for this reaction. Based on this theory proposition, the reaction is initiated by amines that have substituents that donate electrons and possess nucleophilic properties. First, the amine stabilizes the cationic intermediate B, which is converted to intermediate A, and finally during catalyst regeneration.

Conclusions

To sum up, the procedure outlined in this work provides an efficient, economical, and eco-friendly way to synthesize *β*-enaminones and *β*-enaminoesters. The effectiveness of this process depends on using $ZnAl_2O_4@ZnO$ as a heterogeneous, recyclable, and stable catalyst. This procedure facilitates the regio- and chemoselective condensation of several dicarbonyl compounds and diamines. Key advantages of this approach include high yields of desired products, solvent-free conditions, and broad substrate compatibility, making it a valuable complement to existing synthetic methods. In addition, the ability to recycle the catalyst without significant loss of efficiency enhances the sustainability and economics of this method, making it attractive for both industrial and research applications.

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