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Original Research Article

ZnO Nanoparticles: A Highly Efficient and Recyclable Catalyst for Tandem Knoevenagel-Michael-Cyclocondensation Reaction

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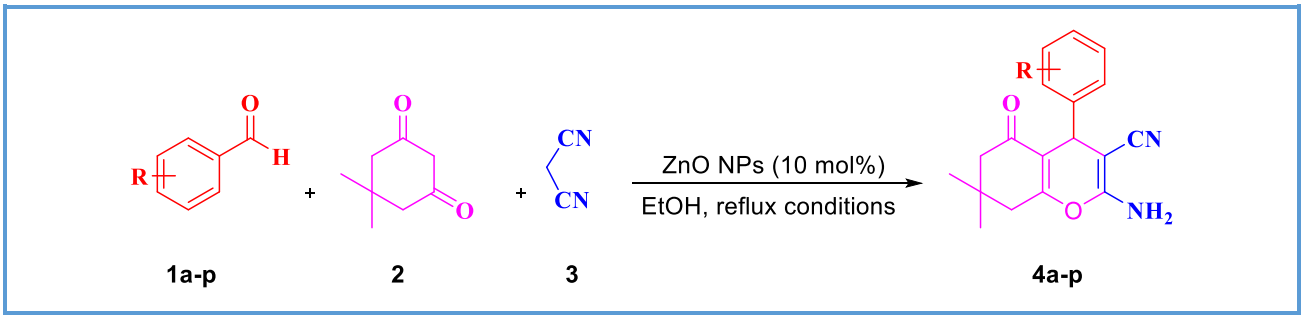
ABSTRACT

In this study, Zinc oxide (ZnO) nanoparticles have been synthesized as a new recyclable solid acid catalyst. Techniques such as FE-SEM, TEM, and XRD were used to characterize as prepared nanocatalyst. Then, the catalyst was used for one-pot three components synthesis of Tandem Knoevenagel-Michael-Cyclocondensation Reaction from various aldehydes, dimedone, and malononitrile in ethanol under reflux conditions. The attractive features of this process are easy work-up, reusability of the catalyst, excellent yields, short reaction times, and mild reaction conditions.

Graphical Abstract



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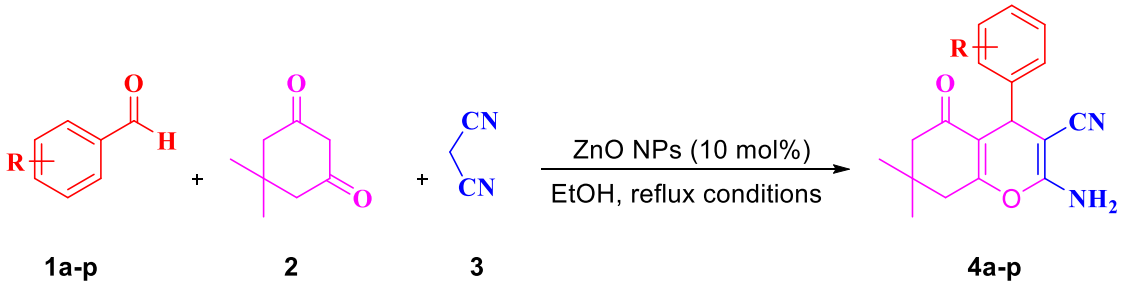
Introduction

MCRs have been of great interest to many chemists and today have a special place in organic and medicinal chemistry. In general, in these reactions, more than two materials are involved and form a product whose structure contains most of the atoms that make up the raw materials. These reactions are known as multi-component ones. MCRs have some advantages such as low reaction time, good efficiency of product, simple deletion of them, and having atom economic. We should pay attention to this fact that many MCRs could not be performed without a catalyst and should be used to carry out reactions a catalyst [1-3].

Transition metal oxide nanoparticles, specifically zinc oxide nanoparticles (ZnO NPs) with high surface to volume ratio has been widely used in organic synthesis reactions. ZnO NPs have received considerable attention as easy to handle, low cost, non-toxic, high reactive, inexpensive, and eco-friendly for various organic transformations [4-8].

Pyrans derivatives are potentially important structural units in heterocyclic chemistry that exhibit various omnipresent biological and pharmacological properties such as anti-inflammatory, antibacterial, antimicrobial, anti-HIV drug, antifungal, antitumor, spasmolytic, anti-rheumatic drugs, and anti-anaphylactic diuretic. Thus, the synthesis of pyran derivatives has attracted great attention because of their wide applications [9-13].

Herein, we report an eco-friendly protocol for the synthesis of pyran derivatives from various aldehydes, malononitrile, and dimedone in the presence of ZnO NPs, as a new recyclable solid acid catalyst (Scheme 1).



Scheme 1. Synthesis of pyran derivatives catalyzed by ZnO NPs

Experimental

General procedure

A mixture of aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), and ZnO NPs (10 mol%) in ethanol was stirred under reflux conditions. After completion of the reaction, the mixture was filtered to remove the catalyst and the crude product was purified by recrystallization from EtOH to obtain the pure compound.

Results and Discussion

In this study, ZnO nanoparticles have been synthesized via a simple procedure [14], and characterization of ZnO nanoparticles carried out by FE-SEM, TEM, and XRD. Then, an efficient and simple method for the Tandem Knoevenagel-Michael-Cyclocondensation Reaction was introduced from various aldehydes, dimedone, and malononitrile in the presence of ZnO catalyst.

Figure 1 indicates the result of FE-SEM and TEME of ZnO nanoparticles to investigate their surface morphology and particle size. The SEM image indicated that ZnO nanoparticles have an

average size below 25 nm (Figure 1a). As seen in Figure 1b, the TEM image demonstrates that the presence and shapes of irregular particles were coexisted with spherical particles.

The XRD pattern of ZnO nanoparticles, displayed in Figure 2, has nine distinct peaks for ZnO nanoparticles in the regions of (100) 31.74, (002) 34.41, (101) 36.15, (102) 47.58, (110) 56.55, (103) 62.81, (200) 66.29, (112) 67.85, and (201) 69.12. This pattern shows that pure ZnO nanoparticles have a hexagonal wurtzite structure, and all the diffraction peaks agree with the reported JCPDS data.

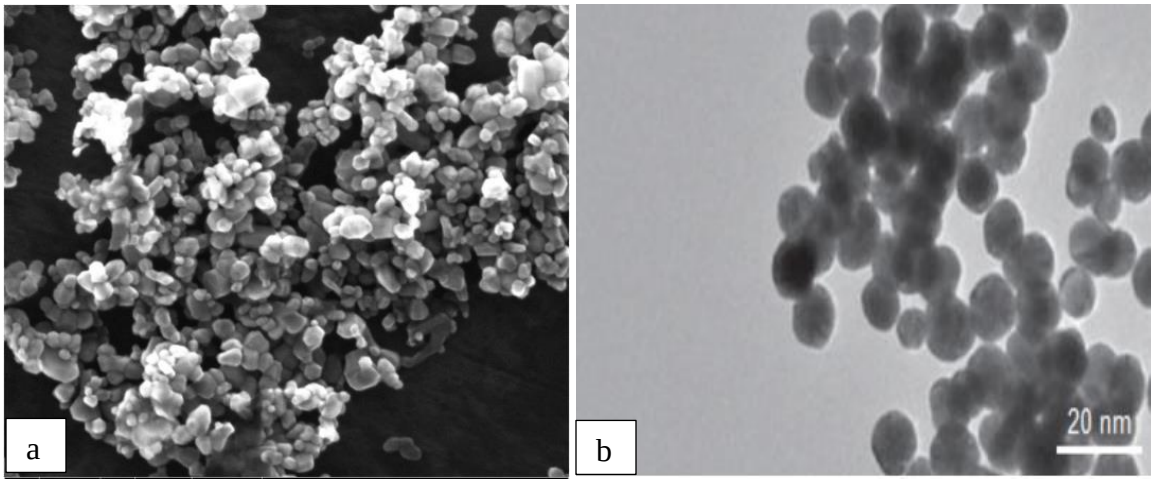


Figure 1. a) SEM image and b) TEM image of ZnO nanoparticles

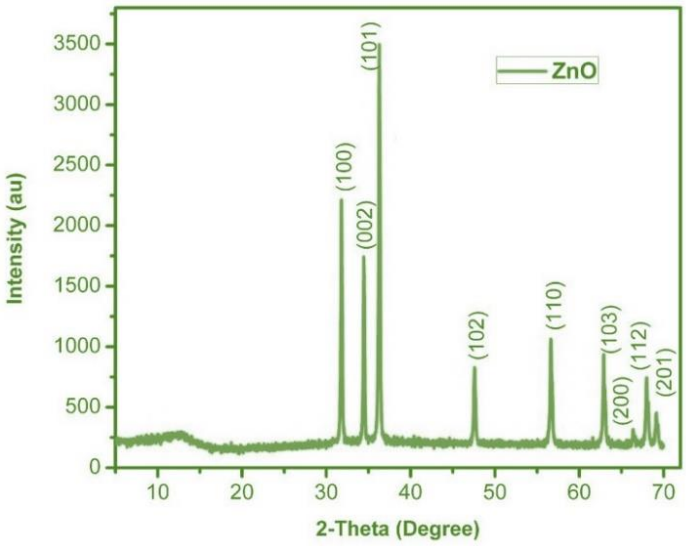


Figure 2. XRD pattern of ZnO nanoparticles

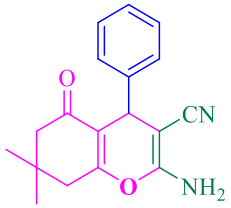
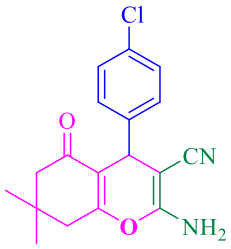
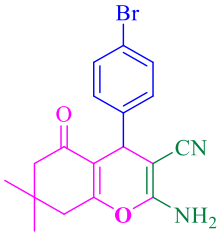
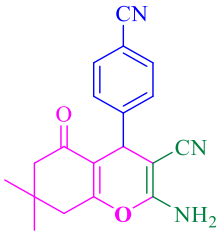
According to the above modified condition, we have synthesized various derivatives of pyran derivatives **4a-p** using various aldehydes **1a-p**, dimedone **2,** and malononitrile **3** with good to excellent yields (89-98%) (Table 1). Briefly, aromatic aldehydes bearing both electron-donating and electron-withdrawing groups can successfully produce ZnO NPs in high yields and short reaction times (1-2.5 hrs).

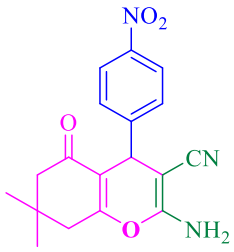
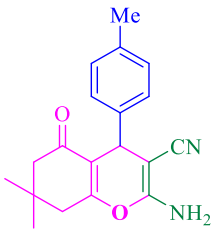
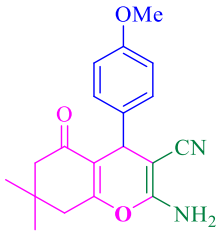
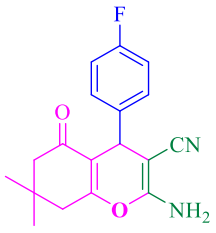
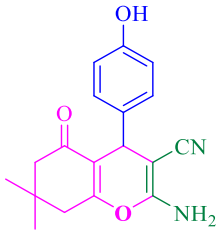
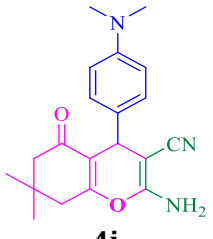
Catalyst activity

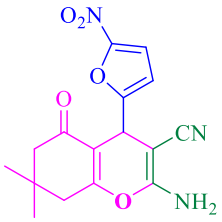
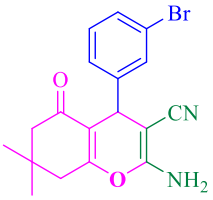
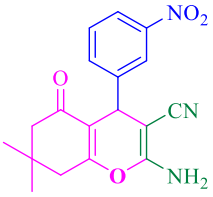
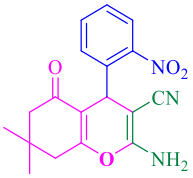
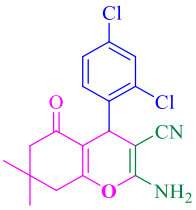
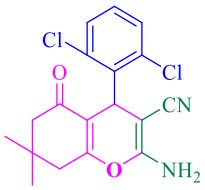
To optimize reaction conditions, the condensation of 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1 mmol) was chosen as the model reaction. The model reaction was investigated under various conditions such as the amount of catalyst, solvent, time, and temperature. The best condition for model reaction is ethanol (2 mL) under reflux conditions using 10 mol% of ZnO NPs after 1 h.

The important point in the application of oxide nanoparticles is reusability of catalyst. Therefore, the condensation of 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1 mmol) in the presence of 10 mol% of ZnO NPs in ethanol under reflux conditions was chosen as model reaction. After completion of the reaction, the mixture was filtered and the catalyst was washed with $CHCl_3$. The results confirmed the stability and efficiency of ZnO NPs at least 5 times and showed no considerable decrease of catalytic activity (Figure 3).

Table 1. Reaction scope[a]

Entry	Products	Time (h)	Yield (%)[b]	M.p (°C) Found	M.p (°C) Reported
1	 **4a**	1	94	229-231	233-235 [15]
2	 **4b**	1.2	96	212-214	214-216 [15]
3	 **4c**	1.2	95	218-220	221-223 [15]
4	 **4d**	1	98	226-228	224-227 [15]

5	 **4e**	1	96	177-179	179-181 [15]
6	 **4f**	2	92	215-217	218-220 [15]
7	 **4g**	2	94	199-201	200-202 [15]
8	 **4h**	1.2	94	189-191	187-188 [15]
9	 **4i**	1.5	91	223-225	225-228 [15]
10	 **4j**	2	93	219-221	182-184 [15]

11	 **4k**	1	91	153-155	154-156 [15]
12	 **4l**	1.5	94	222-224	215-217 [15]
13	 **4m**	1.2	92	210-212	212-213 [15]
14	 **4n**	1	91	218-220	222-223 [15]
15	 **4o**	2.5	90	175-177	177-178 [15]
16	 **4p**	2.5	89	246-248	248-250 [15]

[a] Various aldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol) in the presence of ZnO NPs (10 mol%) in ethanol under reflux conditions

[b] Isolated yield

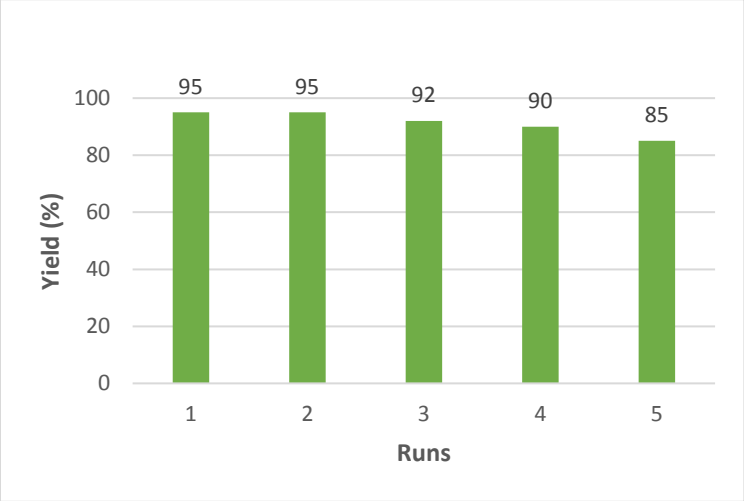


Figure 3. Reusability of ZnO NPs

Conclusion

In summary, ZnO NPs was used in the Tandem Knoevenagel-Michael-Cyclocondensation Reaction of various aldehydes with malononitrile and dimedone. The results showed that ZnO NPs have high catalytic activity, the reaction products were obtained at a nearly quantitative yield. Easy work-up procedure, reusability of the catalyst, excellent yields, short reaction times, and mild reaction conditions are the attractive features of this process.

Conflict of Interest

No potential conflict of interest was reported by the authors.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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