



REGULAR ARTICLE

# Highly active zinc oxide-supported lithium oxide catalyst for solvent-free Knoevenagel condensation

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**Abstract.** Li<sub>2</sub>O/ZnO catalyst was prepared by wet impregnation method and characterized by XRD, SEM, EDX, FTIR, BET surface area and UV-Vis diffuse reflectance spectroscopy. This study revealed a decrease in average particle size and change in the shape of the particles when Li<sub>2</sub>O was supported on ZnO. The activity of ZnO-supported lithium oxide catalyst was tested for Knoevenagel condensation of a variety of aromatic aldehydes with malononitrile and ethyl cyanoacetate at room temperature under solvent-free condition. The reaction was completed in a very short time with yields above 90% and the catalyst presented excellent reusability without any loss in the activity.

**Keywords.** ZnO-supported lithium oxide; Wurtzite structure; Activity; Knoevenagel condensation; Aromatic aldehyde.

## 1. Introduction

The formation of carbon-carbon bond is of great importance to prepare derivatives from carbonyl compounds and active methylene compounds. Knoevenagel condensation is such a reaction extensively used in the synthesis of compounds having pharmacological and biological significance.<sup>1,2</sup> Coumarin and its derivatives used in the preparation of cosmetics, perfumes, and pharmaceuticals are synthesized by Knoevenagel condensation.<sup>3</sup> This reaction is catalyzed by bases like ammonia and their salts, pyridine, piperidine, and a primary amine, secondary amine, tertiary amine and their salts.<sup>4-6</sup> The homogeneous base catalysts require a higher temperature. They render unwanted side reactions and tedious workup procedure and cause difficulty in their recovery from the reaction mixture after the reaction is completed. These soluble liquid bases catalysts must be dispensed with solid bases. Further, the reaction should be performed in solvent-free condition or with water as a medium to accomplish chemical synthesis in a green protocol to increase product yield with greater selectivity.<sup>7,8</sup>

In the past decade, Lewis's acids,<sup>9-11</sup> modified inorganic solids,<sup>12,13</sup> copper metal,<sup>14</sup> resins,<sup>15-17</sup> and phase-transfer agents,<sup>18</sup> have been introduced as new catalysts for this reaction. Microwave and infrared irradiations, ultra-sound and grinding methods have also shown their utility in the Knoevenagel condensation under solvent-free conditions shortening the reaction times and easy workup.<sup>19-25</sup> Sulphated Zirconia,<sup>26</sup> and Ionic Liquids are the other reported catalysts.<sup>27</sup> Solid catalysts and solvent-free condition (or water as reaction medium) lead to the green synthetic protocol for this reaction. Further, the solid catalyst could be easily separated and reused and sometimes, it might even enable higher selectivity and product yield.<sup>7,8</sup> In recent times inorganic solids having acid-base properties are extensively explored in organic synthesis.<sup>28,29</sup> Inorganic oxides with different particle size can be synthesized which will possess different surface properties and used in organic reactions.<sup>30</sup> Solid acid catalysts were employed extensively but, solid bases were less explored in organic transformation.

Low cost, environmental compatibility makes it a potential catalyst in organic synthesis. Nanosize ZnO

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exhibits higher catalytic activity due to its increased surface area and surface defects.<sup>31-34</sup> Modification of surface properties of ZnO by adding other species received much attention due to enhancement of electronic properties and photocatalytic activity.<sup>35</sup> The excellent activity of ZnO reported for several organic transformations spurred our interest in the preparation of ZnO supported system having basic properties. In view of this, an attempt is made to prepare lithium oxide supported on ZnO and its catalytic activity is evaluated for Knoevenagel condensation in a solvent free condition. Several catalysts and methods are available to synthesize olefin derivatives from the condensation of carbonyl compounds with active methylene compounds. In spite of this, the Knoevenagel reaction is revisited because of its simplicity and efficacy in producing a higher amount of olefin derivatives at ambient conditions. Herein, we present the results of Knoevenagel condensation of an aromatic and heteroaromatic aldehyde with malononitrile and ethyl cyanoacetate at room temperature under solvent-free conditions. The  $\text{Li}_2\text{O}/\text{ZnO}$  catalyst exhibited very high activity.

## 2. Experimental

### 2.1 Catalyst preparation

**2.1a Preparation of ZnO:** Zinc acetate dihydrate (12 g) was dissolved 100 mL of distilled water. The pH of the solution was 6.5. To it ammonia solution (5 N) was added drop-wise under continuous stirring using a magnetic stirrer with the solution became slightly alkaline. Ammonia present in its precipitate was removed by washing with distilled water and oven-drying for 24 h at 150 °C. The dried solid was cooled to room temperature, powder and then, calcined at 600 °C to get pale yellow ZnO powder.

**2.1b Preparation of 5%  $\text{Li}_2\text{O}/\text{ZnO}$ :** 2.482 g of anhydrous lithium nitrate was dissolved in 10 mL of distilled water. 5 g of the above-prepared zinc hydroxide powder was added to it. A water bath was used to evaporate the solvent by continuous stirring. The resultant solid was calcined at 600 °C for 6 h.

**2.1c Catalyst characterization:** An XRD 7000 Shimadzu instrument was used for the powder X-ray diffraction patterns of ZnO and  $\text{Li}_2\text{O}/\text{ZnO}$  samples. The scanning range was from 10° to 80° scan speed was 2 deg/min, sampling pitch was 0.0200 deg and pre-set time was 60 sec. The average

crystallite size of the particle was determined using the Debye-Scherrer equation.

A Hitachi model SEM-EDS S3700N instrument was used at an applied voltage of 15.0 kV for scanning electron microscopy (SEM) analysis.

A BRUKER OPTICS model: TENSOR 27 spectrometer was used to record FTIR spectra of the catalyst at ambient conditions and the spectra were scanned using self-supporting KBr pellets containing the catalyst samples.

Brunauer–Emmett–Teller (BET) surface areas of the catalyst sample was determined from nitrogen adsorption-desorption isotherms measured at – 193 °C using a Quanta chrome autosorb system.

UV–vis spectrophotometer (V650, JASCO) was used for UV–Vis diffuse reflectance spectral (DRS) measurements in the range of 200–800 nm. The reflectance standard used was  $\text{BaSO}_4$ .

**2.1d Catalytic activity:** In a typical experimental procedure, a mixture of aromatic aldehyde (10 mmol) and active methylene compound (10.2 mmol) was taken in a 25 mL round-bottomed flask and 0.1 g of the catalyst was added. The reaction mixture was stirred under the solvent-free condition at room temperature. The progress of the reaction was monitored by TLC and the complete disappearance of aldehyde was treated as completion of the reaction. The reactions were also carried in an aqueous medium using 10 mL of water. The catalyst was separated from the reaction mixture after the completion of the reaction by filtration. The mixture was extracted with ether. The organic layer was dried over sodium sulphate and the solvent was removed under vacuum using a rotator-evaporator. The product was subjected to silica gel column chromatography using ethyl acetate and petroleum ether in a 1:9 ratio as eluent to get pure product.

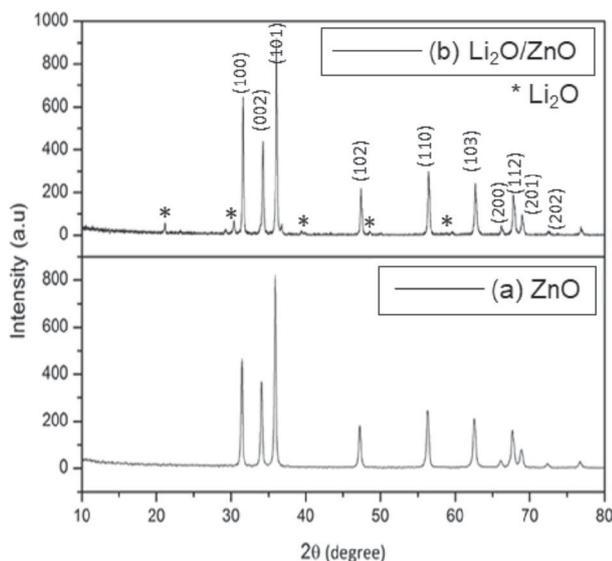
The products were analyzed by determining isolated yields quantitatively and qualitatively by NMR and IR spectroscopy (Figures S1–S18, Supplementary Information).

## 3. Results and Discussion

### 3.1 XRD analysis

The XRD patterns of the calcined samples of pure ZnO and  $\text{Li}_2\text{O}/\text{ZnO}$  in the  $2\theta$  range of 10°–80° are shown in Figure 1.

All the peaks in the XRD pattern of ZnO coincided with the wurtzite structure of ZnO (JCPDS Data Card



**Figure 1.** XRD pattern of (a) pure ZnO and (b)  $\text{Li}_2\text{O}/\text{ZnO}$ .

No: 36-1415). There was no considerable change in the X-ray diffraction pattern upon adding dopant lithium oxide to ZnO except for some increase in the intensity of the peaks indicating an increase in crystallinity of ZnO. No peaks at  $2\theta = 33^\circ$  observed corresponding to crystalline oxides of lithium. Low intensity, new peaks observed below  $2\theta$  of  $30^\circ$  may indicate that a small fraction of lithium is present as its carbonate species. Thus, most of the dopant lithium is in the ZnO lattice but not in the interstitial position as lithium is used in low concentration. The existence of secondary phases cannot be excluded due to the limitation of the characterization technique. This can be attributed to the formation of the solid solution of ZnO with lithium. These results agree with the literature.<sup>35,36</sup> The crystalline domain diameter ( $D$ ) was obtained from XRD peaks using the Scherrer's equation. Average crystallite size of ZnO and  $\text{Li}_2\text{O}/\text{ZnO}$  calculated from Scherrer's formula was 27.7 nm. There is no reduction in crystallite size due to distortion in ZnO lattice by foreign impurity<sup>35</sup> but the catalytic activity towards Knoevenagel condensation at room temperature was enhanced enormously. This might be due to changes in their morphologies, crystallite size, surface microstructures, and the creation of more basic sites either in the bulk or on the surface of the modified ZnO particles. In the present scheme, the reaction was completed in a very short reaction time with  $\text{Li}_2\text{O}/\text{ZnO}$  when compared to pure ZnO. The activity of  $\text{Li}_2\text{O}/\text{ZnO}$  was several folds greater than its pure support ZnO towards the Knoevenagel reaction under solvent-free conditions.

### 3.2 FT-IR analysis

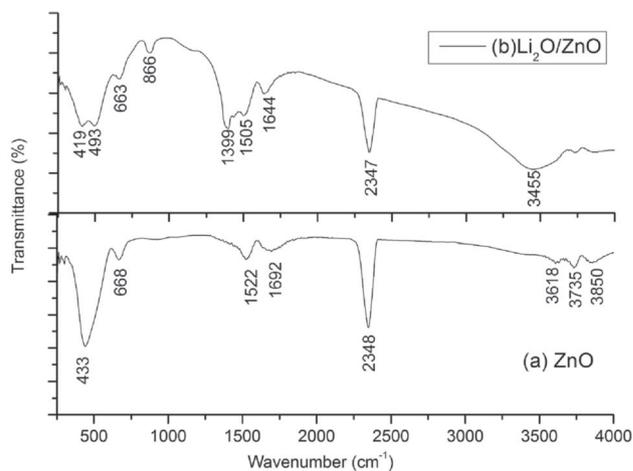
FTIR spectroscopy is a very useful tool for investigating the vibrational properties of synthesized materials. The FTIR spectra of pure ZnO and lithium oxide supported on ZnO calcined at  $600^\circ\text{C}$  are as shown in Figure 2.

The peaks at  $433\text{ cm}^{-1}$  and  $668\text{ cm}^{-1}$  for ZnO are the characteristic absorption bands of Zn-O bonds. Weak peaks at  $1522\text{ cm}^{-1}$  and  $1692\text{ cm}^{-1}$  are attributed to symmetric and asymmetric C=O bond vibrations, respectively. The absorption peaks appearing at  $2348\text{ cm}^{-1}$  is due to the absorption of atmospheric  $\text{CO}_2$  by metallic cation. The peaks in the range of  $3600$  to  $3900\text{ cm}^{-1}$  are attributed to water molecules adsorbed on ZnO. The FTIR and XRD results show the high purity of the obtained ZnO.

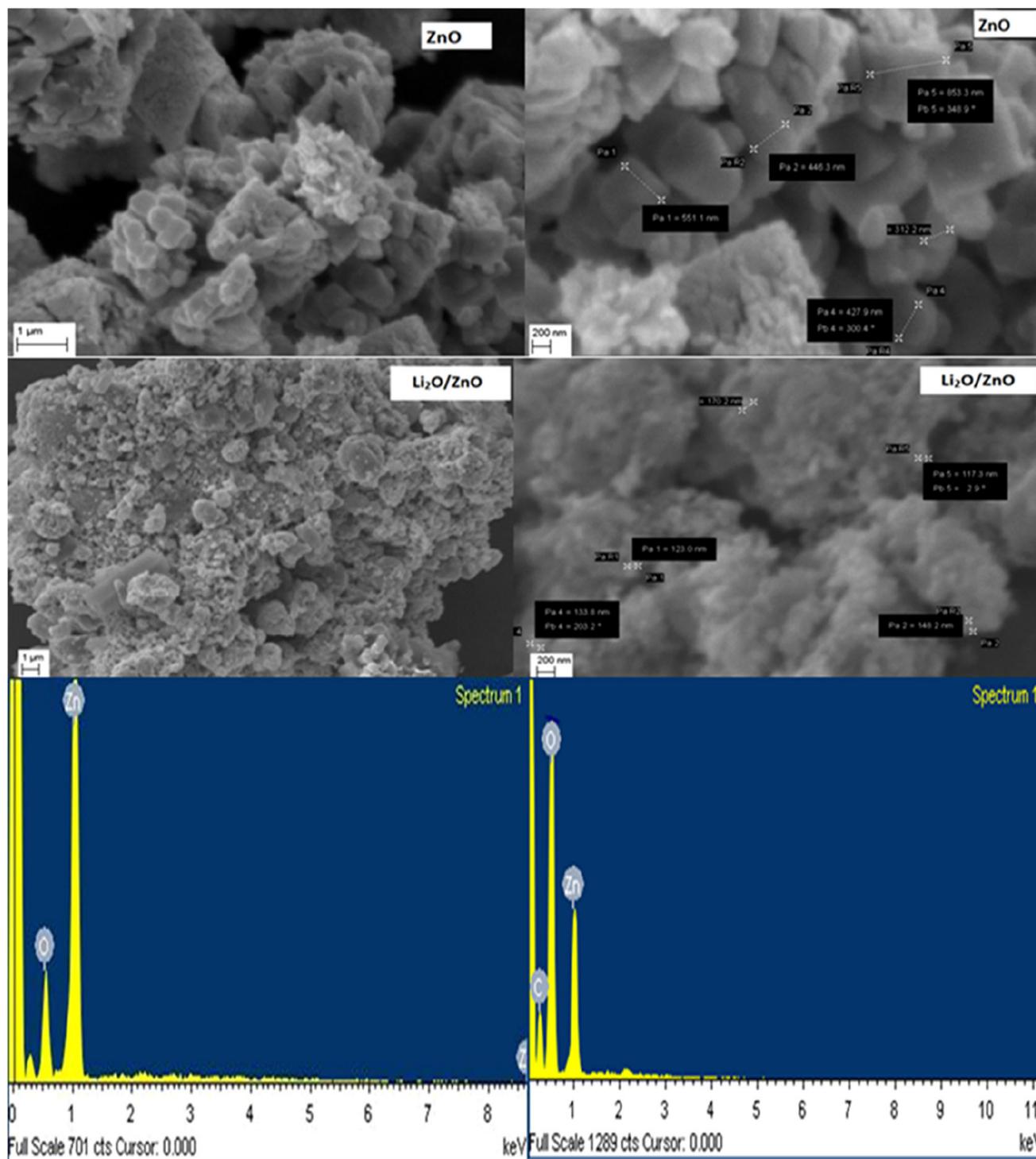
Figure 2(b) is a typical FTIR spectrum of  $\text{Li}_2\text{O}/\text{ZnO}$ . The peak observed at  $433\text{ cm}^{-1}$  for ZnO got shifted to  $419\text{ cm}^{-1}$  for  $\text{Li}_2\text{O}/\text{ZnO}$  and the peak at  $668\text{ cm}^{-1}$  is shifted to  $663\text{ cm}^{-1}$ . The additional peaks observed in the FTIR spectrum of lithium modified ZnO at  $493\text{ cm}^{-1}$  is corresponded to the absorption band of Li-O and the peak at  $866\text{ cm}^{-1}$  is probably due to Li-O-Zn. The broad absorption peak at  $3455\text{ cm}^{-1}$  can be attributed to the characteristic absorption of hydroxyl groups present in the catalyst. The results agree with the literature data.<sup>37,38</sup>

### 3.3 SEM-EDS analysis

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectra (EDS) of both pure and lithium oxide modified ZnO are as shown in Figure 3.



**Figure 2.** FT-IR spectra of (a) pure ZnO and (b)  $\text{Li}_2\text{O}/\text{ZnO}$ .



**Figure 3.** Top: SEM images of pure ZnO, middle: SEM images of  $\text{Li}_2\text{O}/\text{ZnO}$  and bottom: EDS images of pure ZnO and  $\text{Li}_2\text{O}/\text{ZnO}$ .

The topographic study of the sample and determination of the size and shape of the particles can be investigated using SEM. Figure 3 shows the SEM images of ZnO (3a) and  $\text{Li}_2\text{O}/\text{ZnO}$  samples. The morphologies of the ZnO and lithium oxide supported

on ZnO particles are different. From SEM photographs it is clear that lithium oxide supported on ZnO particles are smaller in size compared to pure zinc oxide. Pure ZnO exhibits random sphere and plate-like shape morphology.  $\text{Li}_2\text{O}/\text{ZnO}$  sample shows the formation of

nanosphere bundles due to a high degree of aggregation and agglomeration.

Energy-dispersive X-ray spectra of both the catalysts showed the elemental composition. The element lithium was not identified in the EDS of  $\text{Li}_2\text{O}/\text{ZnO}$ . But FTIR of  $\text{Li}_2\text{O}/\text{ZnO}$  (Figure 2b) shows a vibrational band corresponding to Li-O and moreover the catalyst is more active than pure ZnO. This suggests the presence of lithium oxide in the ZnO lattice. We did not observe the presence of any other foreign element in the compounds.

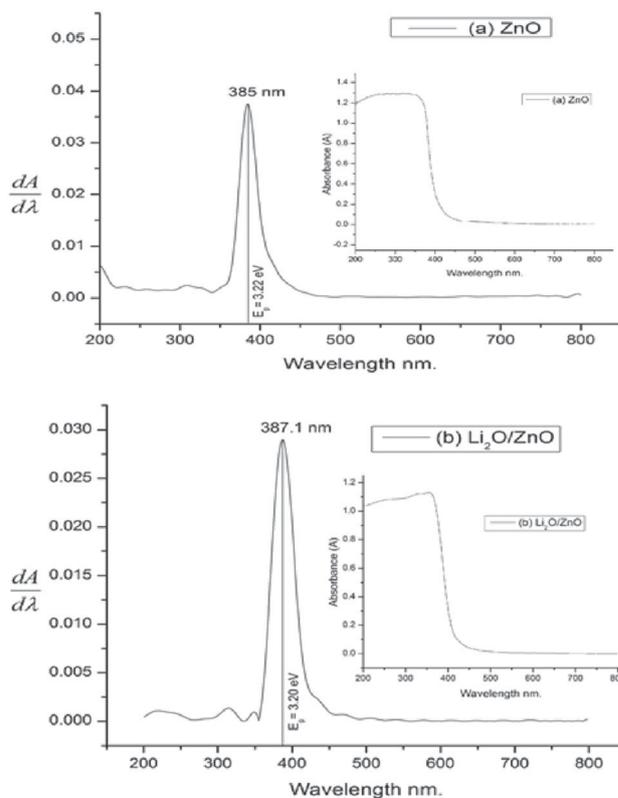
### 3.4 UV-Vis diffuse reflectance spectra

Zinc oxide is an *n*-type metal oxide semiconductor with wide bandgap energy at room temperature. The UV-Vis diffuse reflectance spectra (UV-vis-DRS) of ZnO and  $\text{Li}_2\text{O}/\text{ZnO}$  in the range 200–800 nm are shown in Figure 4.

From Figure 4(a) the absorption maximum of pure ZnO sample appears at  $\lambda = 385$  nm (bandgap of 3.22 eV), whereas the absorption maximum of  $\text{Li}_2\text{O}/\text{ZnO}$  sample appears at  $\lambda = 387.1$  nm (band gap of 3.20 eV) (Figure 4(b)). From the above data, it is clear that the absorption maxima of zinc oxide shifted slightly towards a longer wavelength upon the impregnation of lithium oxide onto the ZnO lattice. The energy gap increases on adding dopant donors to ZnO and decreases on adding acceptors. Like in photocatalysis where the increase in zinc vacancies accompanied by oxygen vacancies is responsible for the higher activity, the dopant lithium in zinc oxide decreases band gap energy and is responsible for higher activity by abstracting hydrogen from the methylene group.<sup>38</sup>

BET surface area of ZnO is  $5 \text{ m}^2/\text{g}$  and of  $\text{Li}_2\text{O}/\text{ZnO}$  is  $20 \text{ m}^2/\text{g}$ . There is a fourfold increase in the surface area after the incorporation of the lithium into the zinc oxide lattice. This can be correlated to a decrease in particle size observed from SEM for lithium oxide supported on ZnO catalyst.

The solvent effect on the model reaction between benzaldehyde and malononitrile in presence of various solvents (10 mL) are presented in Table 1. The reaction occurs smoothly with malononitrile and ethyl cyanoacetate under similar conditions but the reaction is slow with ethyl cyanoacetate. Higher activity with malononitrile is due to the presence of two electron-withdrawing groups.  $\text{Li}_2\text{O}/\text{ZnO}$  catalyst was investigated for the base catalysed Knoevenagel condensation of various aldehydes with malononitrile and ethyl cyanoacetate (Scheme 1) and the results are presented



**Figure 4.** (a). UV-vis-DRS of pure ZnO. (b) UV-vis-DRS of  $\text{Li}_2\text{O}/\text{ZnO}$ .

in Table 2 and Table 3. The catalytic reaction was performed at room temperature under solvent-free condition and in the aqueous medium (10 mL) by taking active methylene compound slightly in excess. The catalyst is novel and efficient for Knoevenagel condensation with yields reaching >90% under solvent-free condition but the time taken for completion of the reaction is increased and the yields decreased in

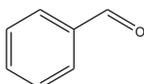
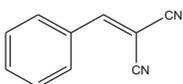
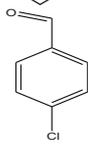
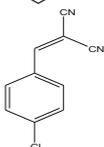
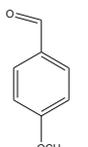
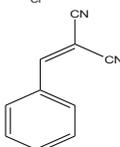
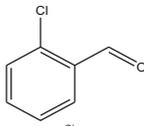
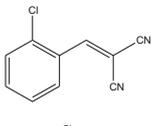
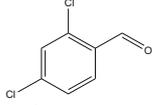
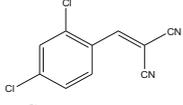
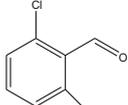
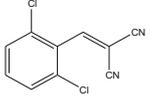
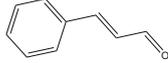
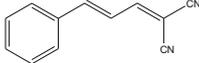
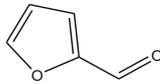
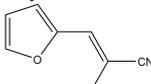
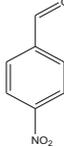
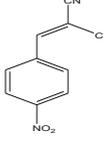
**Table 1.** Influence of solvent on activity of  $\text{Li}_2\text{O}/\text{ZnO}$  catalyst for Knoevenagel condensation of benzaldehyde with malononitrile.

Entry	Solvent	Time (min)	<sup>a</sup> Yield (%)
1	Ethyl acetate	360	88
2	Acetonitrile	270	92
3	DMF	60	90
4	DMSO	25	93
5	Methanol	7	96
6	Water	05	95
7	Solvent free	4	93

Reaction condition: Catalyst (0.1 g), benzaldehyde (10 mmol) and malononitrile compound (10.2 mmol) were stirred at room temperature in various solvents (10 mL) and in a solvent free condition.

<sup>a</sup> Isolated Yields.

**Table 2.** Knoevenagel condensation of malononitrile and aldehyde catalysed by 5% Li<sub>2</sub>O/ZnO.

Sl. No.	Reactant	Product	Aqueous medium		Without solvent	
			Time (min)	<sup>b</sup> Yield (%)	Time (min)	<sup>c</sup> Yield (%)
1			05	95	4	93
2			11	92	3	91
3			9	95	05	94
4			07	90	2	93
5			12	87	3	92
6			03	96	1	94
7			7	93	1	95
8			02	92	02	93
9			02	95	1	96

Reaction condition. Catalyst (0.1 g), aldehyde (10 mmol) and malononitrile compound (10.2 mmol) stirred at room temperature in aqueous medium (10 mL) and under solvent free condition.

<sup>b,c</sup>Isolated yields.

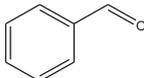
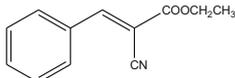
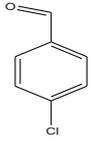
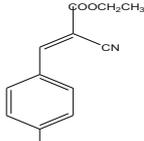
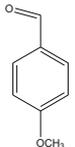
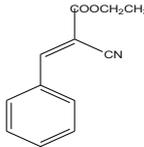
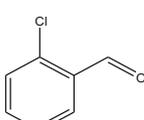
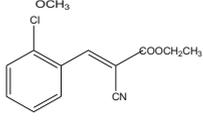
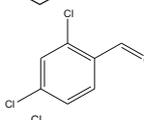
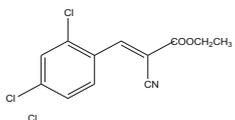
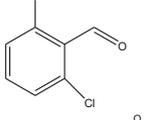
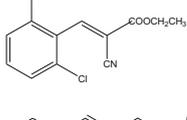
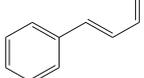
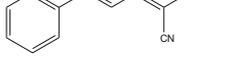
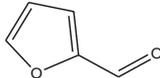
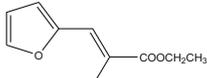
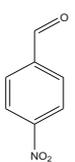
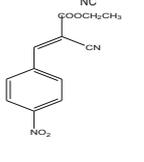
presence of water and other solvents. It is noteworthy to mention that heteroaromatic compound is also very reactive.

Knoevenagel condensation is a base catalysed reaction and depends on basic sites present on the surface of the catalyst. ZnO oxide possesses both acid and base sites. The incorporation of lithium oxide probably enhances surface basic sites by blocking surface acid sites. The higher catalytic activity of Li<sub>2</sub>O/ZnO can be attributed to the increasing basicity

of the catalyst. The mechanism involves the steps of formation of carbanion initially by abstraction of a proton from acidic methylene group by the catalyst followed by the attack on carbonyl electron acceptor centre.<sup>34</sup>

In Table 4 Knoevenagel condensation of benzaldehyde with malononitrile catalysed by various catalysts for comparison is given. Lithium oxide supported on zinc oxide is found to be superior among the catalysts reported in the earlier works.

**Table 3.** Knoevenagel condensation of ethyl cyanoacetate and aldehyde catalyzed by 5% Li<sub>2</sub>O/ZnO at room temperature in an aqueous medium, under solvent-free condition.

Sl. No.	Aldehyde	Product	Aqueous medium		Without solvent	
			Time (hours)	<sup>d</sup> Yield (%)	Time (minutes)	<sup>e</sup> Yield (%)
1			4	87	90	94
2			14	92	75	92
3			20	89	180	91
4			04	85	60	94
5			10	90	40	93
6			02	92	13	95
7			1	86	08	93
8			02	95	05	95
9			3	94	20	96

Reaction condition: Catalyst (0.1 g), aldehyde (10 mmol) and ethyl cyanoacetate compound (10.2 mmol) stirred at room temperature in an aqueous medium (10 mL) and under solvent-free condition.

The reusability of Li<sub>2</sub>O/ZnO catalyst was investigated. The catalyst was recovered after completion of the reaction by filtration, washed with ethanol, and dried in the oven at 100 °C. The catalyst was found to be active in four cycles with marginal loss in activity (Figure 5). The marginal loss in the activity may probably be due to poisoning of the surface of the catalyst by organic impurities.

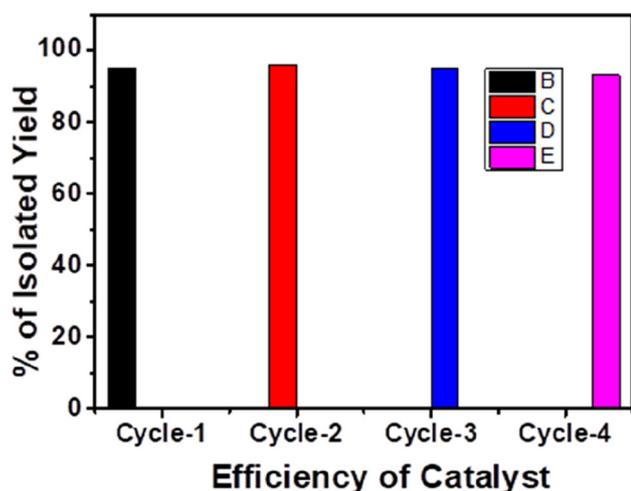
#### 4. Conclusions

In conclusion, a novel catalyst has been developed for the synthesis of olefin derivatives in a short reaction time. Decreases in the particle size, and band gap energy and increases in the surface area and basic properties of ZnO was observed for the Li<sub>2</sub>O/ZnO catalyst. Lithium oxide supported on zinc oxide catalyst exhibits very high activity in Knoevenagel

**Table 4.** Knoevenagel condensation of benzaldehyde and malononitrile catalysed by various catalysts for comparison.

Catalyst	Temperature	Time	Yield (%)	Reference
ZnCl <sub>2</sub> (anhyd.)	100 °C	10 min	90.9	9
LiBr	Reflux (water), 80 °C	10 min	90	10
BiCl <sub>3</sub>	80 °C	20 min	75	11
Zn-NaY	60 °C	8 h	59	12
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	Reflux	180 min	89	26
ZnO	RT	3.5 h	90	34
Li <sub>2</sub> O/ZnO	RT	4 min	93	Present work

<sup>d,e</sup> Isolated yields.

**Figure 5.** Recyclability of the Li<sub>2</sub>O/ZnO catalyst.

condensation of aromatic aldehyde and malononitrile/ethyl cyanoacetate under solvent-free condition. The catalyst can be recovered and reused several times.

### Supplementary Information (SI)

Figures S1-S18 are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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