



# Fly ash supported calcium oxide as recyclable solid base catalyst for Knoevenagel condensation reaction

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## ABSTRACT

A new type of solid base catalyst has been prepared by loading of CaO on thermally activated fly ash, with the aim of being used as heterogeneous catalyst for fine chemical production. The prepared fly ash supported calcium oxide catalyst (FAC) was characterized by FT-IR spectroscopy, X-ray diffraction analysis, Scanning Electron Microscopy and atomic absorption spectroscopy. The catalytic activity of FAC was evaluated by Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate as model test reaction under optimized conditions. The catalyst gave very high conversion (87%) of benzaldehyde to desired product ethyl (*E*)- $\alpha$ -cyanocinnamate with high purity. The catalyst was completely recyclable without significant loss in activity up to three reaction cycles, which confers its stability during reaction unlike commercial catalysts. Moreover this catalyst shows a promising future in providing environmentally clean process for the industrial sector.

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## 1. Introduction

Base catalyzed condensation reactions are synthetically important organic transformation for the preparation of wide variety of condensation products, which are key intermediates in the manufacture of pharmaceutical and fine chemical intermediates [1]. Homogeneous bases such as alkaline oxide, alkaline earth oxides, and hydroxides are widely used as catalysts in organic reactions including isomerizations [2], C–C bond formation [3], additions [4], cyclization, oxidation [5] and condensation [6–8]. Among all condensation reactions, Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate is of great interest as this reaction leads to ethyl (*E*)- $\alpha$ -cyanocinnamate, a well known pharmaceutical and fine chemical intermediates [9]. Commercially this reaction was carried out using various homogeneous base catalysts such as piperidine, amines, ammonia, and ammonium salts, which are corrosive, toxic, nonreusable and also produce neutralization waste [10]. An important step to phase out the problems associated with use of homogeneous bases is the application of product selective and recyclable solid base catalyst in such reactions. A number of solid bases such as KF/Al<sub>2</sub>O<sub>3</sub>, hydrotalcite, KNH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and immines/SiO<sub>2</sub> have been reported in literature for catalyzing several condensation reactions [11–14]. Other heterogeneous catalysts used so far for Knoevenagel condensation reaction are zeolites [15], Al-enriched fluoroapatites and hydroxyapatites [16], clay, calcined hydrotalcite and Al<sub>2</sub>O<sub>3</sub> [6], Cs-exchanged

NaX faujasite zeolite [17], amino based metal organic framework [18], alkali earth oxide supported on alumina [19] and magnesium oxide [20]. Condensation of benzaldehyde with some methylenic compounds viz. ethyl cyanoacetate, ethyl acetoacetate and diethyl malonate has been reported to be catalyzed by a series of lithium, sodium, potassium, rubidium and cesium impregnated on oxide matrices (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Nb<sub>2</sub>O<sub>5</sub>) [21].

The present work elaborates the synthesis of fly ash supported-CaO catalyst to have high basicity and catalytic activity for Knoevenagel condensation reaction to produce ethyl (*E*)- $\alpha$ -cyanocinnamate. Fly ash is a silica enriched material, containing silica, alumina, ferric oxide, calcium oxide and other metal oxide such as Mn<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and inert crystallite phases such as mullite, quartz and magnetite [22], which is being used in the present work as solid support for loading CaO. One of the main constituents of fly ash is silica (54%), having insufficient catalytic activity which was enhanced by loading CaO correspondingly generating CaO–SiO<sub>2</sub> phase with high basicity and sufficient catalytic activity. In the present research work fly ash after loading of CaO has been employed as a novel, noncorrosive, efficient and recyclable solid base catalyst for organic transformations.

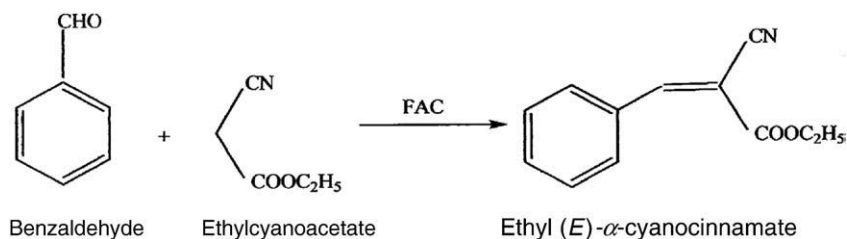
## 2. Experimental procedure

### 2.1. Material

Calcium carbonate (CaCO<sub>3</sub>) (98%), benzaldehyde (99.9%) and ethyl cyanoacetate (99%) were purchased from s. d. Fine Chem. Ltd., India and were used as such. The coal fly ash (Class F type) used in this study was collected from Kota Super Thermal Power Station (Kota, Rajasthan, India). The components of fly ash are SiO<sub>2</sub> (54%),

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**Scheme 1.** The Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate using FAC catalyst.

Al<sub>2</sub>O<sub>3</sub> (21%), Fe<sub>2</sub>O<sub>3</sub> (9%), CaO (1.6%), MgO (0.8%), TiO<sub>2</sub> (1.3%), Na<sub>2</sub>O (4.8%), K<sub>2</sub>O (3.2%) and trace elements (4.0%). The L.O.I (loss on ignition) was found to be 3% on heating fly ash at 900 °C for 3 h.

## 2.2. Preparation of the catalyst

FAC was prepared by loading of calcium oxide on fly ash support. Fly ash support was calcined at 900 °C for 3 h prior to use. 0.25 g CaCO<sub>3</sub> dissolved in hot deionized water was added to 1 g of calcined fly ash in a 250 ml round bottom flask. The mixture was refluxed at 110 °C for 2 days maintaining the temperature. After refluxing, the mixture was filtered and the paste obtained was dried at 120 °C for 24 h followed by calcination at 700 °C for 2 h in order to get CaO from CaCO<sub>3</sub>.

## 2.3. Characterization

### 2.3.1. Physicochemical properties of FAC

The prepared fly ash supported calcium oxide catalyst (FAC) was characterized by different analytical techniques such as XRD, FT-IR, SEM and Flame Atomic Absorption Spectrophotometer, which confirm the presence of CaO on fly ash. The crystallinity and crystallite size of the catalyst was analyzed by X-ray powder diffractometer (Philips X'pert) using CuK $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The sample was scanned in  $2\theta$  range of 0–80° at a scanning rate of 0.04° s<sup>-1</sup>. The FT-IR study of the sample was done by FT-IR spectrophotometer (IRPrestige-21, Shimadzu) in DRS (Diffuse Reflectance Spectroscopy) system by mixing the sample with KBr in 1:20 weight ratio for better resolution. The spectrum was recorded in the range 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The chemical composition of fly ash and amount of Ca present in FAC were analyzed by Flame Atomic Absorption Spectrophotometer (AA-6300, Shimadzu). The detailed

imaging information about the morphology and surface texture of the sample was provided by SEM (Philips XL30 ESEM TMP).

### 2.3.2. Catalytic activity

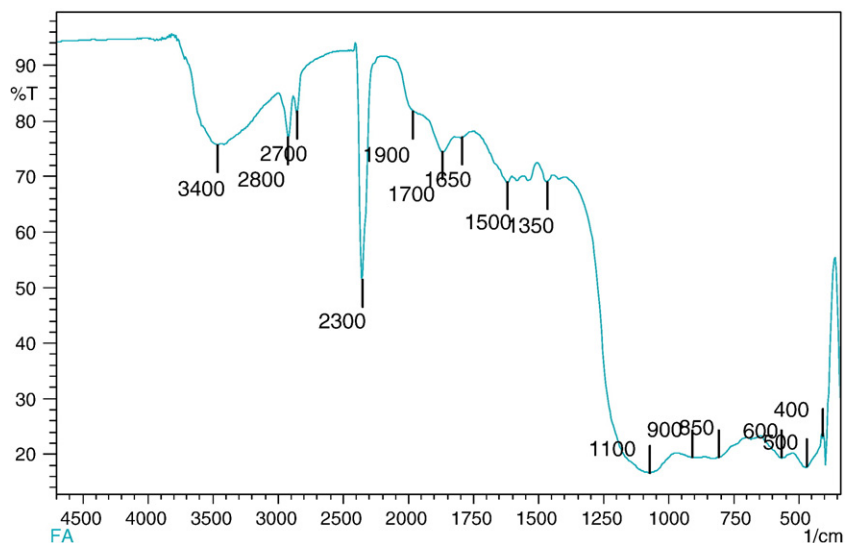
The catalyst FAC was tested by Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate shown as Scheme 1. The reaction was carried out in a liquid phase batch reactor under optimized conditions.

**2.3.2.1. Typical reaction procedure.** In the procedure, benzaldehyde (1.5 g) and ethyl cyanoacetate (1.1 g) (molar ratio of benzaldehyde/ethyl cyanoacetate = 1.5:1) were taken in a 50 ml round bottom flask, equipped with magnetic stirrer and condenser, immersed in a constant temperature oil bath. The solid base catalyst (benzaldehyde/catalyst = 5:1), activated at 700 °C for 2 h prior to the reaction, was added in the reaction mixture. The reaction mixture was heated at required reaction temperature ranging from 40 to 120 °C and time from 30 min to 4 h at atmospheric pressure. After the completion of reaction, the mixture was cooled and filtered to separate the catalyst and was analyzed by gas chromatograph (Dani Master GC) having a flame ionization detector and HP-5 capillary column of 30 m length and 0.25 mm diameter, programmed oven temperature of 50–280 °C and N<sub>2</sub> (1.5 ml/min) as a carrier gas. The conversion was calculated as follows:

$$\text{Conversion (wt\%)} = 100 \times [\text{Initial wt\%} - \text{Final wt\%}] / \text{Initial wt\%}.$$

### 2.3.3. Catalyst regeneration

After completion of the reaction, catalyst was filtered and washed thoroughly with acetone and dried in an oven at 110 °C for 12 h followed by activation at 700 °C for 2 h in static condition prior to the use in next reaction cycle.



**Fig. 1.** FT-IR of FA.

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