Ce$_1$Mg$_x$Zr$_{1-x}$O$_2$ (CMZO): An efficient and eco-friendly solid heterogeneous catalyst for the synthesis of 5-arylidene malononitrile derivatives

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ABSTRACT

An eco-friendly Ce$_1$Mg$_x$Zr$_{1-x}$O$_2$ (CMZO) solid heterogeneous catalyst has been employed for the synthesis of 5-arylidene malononitrile derivatives via Knoevenagel condensation of various aromatic aldehydes and malononitrile in EtOH:H$_2$O at 50-60°C. The catalyst was prepared by simple co-precipitation method and calcined at 500°C. The calcined powder sample was characterized by XRD, FT-IR, SEM and EDS techniques. The catalytic activity results suggest that, the methodology adapted to offer significant improvements in the synthesis of 5-arylidene malononitriles with regards to short reaction times, high yields and the catalyst was successfully reused for three cycles without significant loss of activity.

KEYWORDS

Heterogeneous Catalyst; CMZO; 5-Arylidene Malononitrile; XRD; FT-IR; SEM-EDS.

INTRODUCTION

The synthesis of arylidene derivatives has attracted considerable attention from organic chemists for many years, because many of them have significant biological activity. More over, 5-arylidene malononitrile were reported to be effective anti-fouling agents, uncicides and insecticides. They are important intermediates for the synthesis of various organic compounds[1].

Knoevenagel condensation of carbonyl compounds on molecules containing an active methylene group is an important method for the preparation of substituted alkenes. Several important key products, such as nitriles used in anionic polymerization and a,b-unsaturated ester intermediates employed in the synthesis of several therapeutic drugs, e.g., niphedipine and nitrendipine, etc. have been synthesized via this condensation[12]. Ylidenenitriles have increasing application in industry, medicine, agriculture and biological science, and are precursors to heterocycles[31]. The Knoevenagel condensation reaction is generally catalyzed by bases, acids or catalyst containing both acid-base sites[4]. Numerous acid-base reagents or catalysts and Lewis acids, Ammonium acetate[5], calcined hydrotalcite[6], ionic liquids[7], surfactants[8], CaO[9], AlPO$_4$ -modified Zeolite[10], KF-Al$_2$O$_3$[11], promoted ZrO$_2$[12], Ni-SiO$_2$[13], TiCl$_4$/base[14], ZnCl$_2$[15], CdI$_2$[16]. Most of these methods have not been entirely satisfactory owing to such drawbacks as use of harmful solvents, highly acidic conditions, poor yields, and longer reaction times, hazardous and expensive acid catalyst.

In view of environmental and economical aspects, there is an ongoing effort to replace the conventional catalyst by solid heterogeneous catalyst this is mainly
due to some distinct advantages such as non toxicity, non corrosiveness, ease of handling, less expensive and easy to recover and reuse. Recent decades have witnessed an exponential growth in the applications of heterogeneous catalysis to carry out synthetic transformation as a consequence of its significance in terms of enviro-economical and practical aspects [17].

Recently, mixed metal oxide as a solid heterogeneous catalyst would be an encouraging alternative owing to its easy synthesis and ecofriendliness. The use of mixed metal oxide based catalyst offers several advantages, such as active over a wide range of temperature and more resistant to thermal excursions. A mixed metal oxide represents one of the most important and widely employed categories of solid catalyst, either as active phase or supports. A metal oxide utilized both for their acid-base and redox properties and constitutes the largest family of catalyst in heterogeneous catalysis [18-21]. Metal oxide and mixed metal oxide have been extensively used as a catalysts and catalyst supports for wide variety of reactions [22-29].

By observing such a wide applicability of mixed metal oxide in catalytic reaction and their potential uses, we are encourage to prepare a CMZO solid heterogeneous catalyst by simple co-precipitation method and decided to investigate their catalytic activity in the synthesis of 5-arildene malononitrile derivatives via Knoevenagel condensation. And which have been proved to be excellent.

**EXPERIMENTAL**

**Materials**

All the chemicals used were of synthesis grade re-agents (Merck) and obtained from commercial suppliers and used as such. All products are known compounds and their physical data; IR and \(^1\)H NMR spectra were essentially identical with those of authentic samples.

**Catalyst preparation**

The CMZO catalyst was prepared by simple co-precipitation method. An aqueous solution containing the requisite quantities of ammonium ceric nitrate, zirconyl nitrate and magnesium nitrate were prepared separately by using deionized water and mixed together with constant stirring followed by the addition of 20 ml 5% polyethylene glycol (PEG-400) as a structure directing agent. The molar ratio of (Ce\(^{4+}\), Mg\(^{2+}\), and Zr\(^{4+}\) = 1:0.6:0.4.) This solution was hydrolyzed with 1:1 aqueous ammonia with vigorous stirring until the pH of solution reached to 9 (pH = 9). A yellowish precipitate was formed and the precipitate was allowed to settle down in an electric oven at 60°C for 24 h. The resulting precipitate was filtered and washed with deionized water to remove the nitrates and dried at 120°C for 12 h. Finally, the dried precipitate was crushed in clean mortar to get yellowish fine powder, and obtained pow-dered material was calcined at 500°C for 1h in air atmosphere.

**Catalyst characterizations**

The X-ray powder diffraction patterns of catalyst were recorded on Bruker 8D advance X-ray diffractometer using CuK\(\alpha\) radiation of wavelength = 1.54056 Å°. The IR spectra were recorded on FT-IR spectrometer (JASCO FT-IR/4100) Japan, using dry KBr as standard reference in the range of 4000-500 cm\(^{-1}\). To study the morphology of catalytic material the SEM analyses were carried out with JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA. The elemental compositions of metal in CMZO (1:0.6:0.4) catalyst were examined using energy dispersive spectrophotometer (EDS).

**General procedure for the synthesis of 5-arildene malononitrile**

Mixture of aromatic aldehydes (1mmol) and malononitrile (1mmol) and CMZO (0.1 g) was refluxed in ethanol:water for indicated time as required to complete the reaction (TABLE 1). Upon completion of the reaction, monitored by TLC, the reaction mixture was

| TABLE 1: XRD analysis data of CMZO catalyst calcined at 500°C. |
|----------------------|----------------------|
| h  k  l 2θ (Exp) (Degree) | 2θ (Cal) (degree) | d (Exp) | d (Cal) | Intensity (Exp) |
|----------------------|----------------------|
| 1 1 0 23.702 23.502 | 3.78080 | 3.78231 | 118.02 |
| 1 1 1 28.449 28.544 | 3.13489 | 3.12462 | 637.88 |
| 2 0 0 32.924 33.077 | 2.71828 | 2.70600 | 288.26 |
| 2 2 0 47.676 47.478 | 1.90595 | 1.91343 | 419.13 |
| 3 1 1 56.498 56.336 | 1.62750 | 1.63178 | 396.02 |
| 4 0 0 70.306 70.344 | 1.33787 | 1.33725 | 180.03 |
| 3 3 1 76.673 76.692 | 1.24186 | 1.24160 | 248.17 |
cooled to room temperature. The mixture was filtered off (removed the catalyst and catalyst was washed with methanol for reuse). Upon the evaporation of the solvent, the crude product was recrystallized from ethanol to give the pure product. The authenticity of the products was investigated by comparing their melting points and ¹H NMR spectra with data in the literature.

Spectral data of selected compounds

3h: IR (KBr) - 2208, 2919, 1536, 1356, 946 cm⁻¹. ¹H NMR (δ in DMSO) 3.09 (s, 6 H), 6.85 (d, 2 H), 7.83 (d, 2 H), 8.03 (s, 1 H).

3i: IR (KBr) - 2239, 3052, 1530, 1331, 856. ¹H NMR (δ in DMSO) 8.95 (s, 1 H), 8.33 (d, 1 H), 8.01 (t, 1 H), 7.94 (d, 2 H), 7.90 (t, 1 H).

RESULTS AND DISCUSSIONS

XRD analysis

In order to understand the phase symmetry of the prepared powdered materials a systematic study on the XRD was undertaken. Figure 1 (a) shows XRD pattern of CMZO catalyst, calcined at 500°C for 1h in air atmosphere. The peaks were apparently broad, due to small particle size and poor crystallinity. The highly intense and sharp peaks were obtained at (2θ = 28°, 33°, 47°, 51°, 57°, 59°, 77°) corresponding to the planes of (111), (200), (220), (221), (311), (222), (322), (331) indicating the formation of cubic solid solutions.

FT-IR analysis

From IR spectra it was found that, the broad band in the range 3000-3500 cm⁻¹ are due to the (O-H) vibrations of H₂O absorbed by the powder sample. The bands at 1580 cm⁻¹ are due to the deformation vibration mode of water (δ-OH). Also characteristic peak 1075 cm⁻¹ are attributed to the vibrations of M-O-M (M = Ce, Mg or Zr) bonding. Moreover no characteristic absorption peak are found at 1384 cm⁻¹ it means that, nitrates are completely removed during filtration and washing. In the spectra, we can find the absorption peaks at 860 cm⁻¹, 665 cm⁻¹ and 529 cm⁻¹ are due to stretching and bending mode of vibrations of M-O-M bonding.

SEM analysis

To evaluate morphology of CMZO (1:0.6:0.4) catalyst as shown in Figure 3 The SEM micrograph of CMZO catalyst shows homogeneous agglomeration of particles and was irregular in shape and agglomerated, with an average primary particle size > 1 µm. It was also observed that there is a generation of some porosity, which may be due to addition of 5% PEG as structure directing agent. As can be noted from the micrograph of CMZO all the three metal oxides is strongly interacted and highly dispersed on their surfaces.

The elemental composition of CMZO (1:0.6:0.4) catalyst are shown in Figure 3 represents the elemental distribution of Ce, Mg, Zr, O as 60.10 wt% (22.53 a%), 1.27 wt% (2.75 a%), 19.25 wt% (11.09 a%), and 19.38 wt% (63.63 a%).
To start our investigation to get good experimental conditions, we performed the study of various solvents effect on the course of reaction of 4-chlorobenzaldehyde with malononitrile. This reaction is carried out in various solvents such as water, DMF, Ethanol, Chloroform, Ethanol:Water, Toluene, and best results in terms of yield and time obtained in Ethanol:water. After optimizing the reaction conditions, various aromatic aldehydes reacted very well with malononitrile as active methylene compounds to give the corresponding arylidines in good to excellent yields (Scheme 1). The results are summarized in TABLE 2. As shown in TABLE 2, aromatic aldehydes containing both electron donating or withdrawing groups gave the desired products good to excellent yields.

The use of CMZO as a recyclable catalyst in this reaction allowed us to perform the condensation under mild conditions. In this case, yields were excellent. In order to show the merit of the present work in comparison with some reported procedures, we compared the results of the synthesis of olefinic compounds in the presence of HZSM-5, Proline, RE-NaY zeolite, Ni-SiO₂, and CMZO with respect to the reaction times and yields of the products (TABLE 3). The results show that CMZO promotes the reaction more effectively than HZSM-5. Reaction in the presence of other catalysts in TABLE 3 required longer reaction times.

**TABLE 3: Comparison of synthesis of 5-arylidine malononitrile using different catalysts.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HZSM-5</td>
<td>5-12</td>
<td>60-80</td>
<td>[34]</td>
</tr>
<tr>
<td>2</td>
<td>Proline</td>
<td>Over night</td>
<td>66-100</td>
<td>[35]</td>
</tr>
<tr>
<td>3</td>
<td>RE-NaY zeolite</td>
<td>8-18 (h)</td>
<td>78-100</td>
<td>[36]</td>
</tr>
<tr>
<td>4</td>
<td>Ni-SiO₂</td>
<td>15 (h)</td>
<td>75-100</td>
<td>[13]</td>
</tr>
<tr>
<td>5</td>
<td>CMZO</td>
<td>20-30 (min)</td>
<td>90-95</td>
<td>Present works</td>
</tr>
</tbody>
</table>

*a Refers to the isolated yield

**Scheme 1: Synthesis of 5-arylidine malononitrile catalyzed by CMZO catalyst.**

**Scheme 2: Suggested mechanism for the synthesis of 5-arylidine malononitrile catalyzed by CMZO catalyst.**
cally we believe that, CMZO facilitates both acidic and basic sites \((M^+\text{---}O^-)\), \((M = \text{Metal cation})\) providing good active sites, due to this reaction rate enhances and thereby excellent yields of the products obtained. The probable mechanistic path is given in Scheme 2.

Next, we investigated the reusability and recycling of CMZO catalyst. At the end of the reaction, the catalyst could be recovered by a simple filtration. The recycled catalysts could be washed with methanol and subjected to a second run of the reaction process. To assure that catalysts were not dissolved in methanol, the catalyst was weighted after filtration and before using and reusing for next reaction. The results show that these catalysts are not soluble in methanol. In TABLE 4, the comparison of efficiency of CMZO in the synthesis of 3c after three times is reported. As it is shown in TABLE 4, recovered CMZO catalyst afforded consistent yields in the first, second and third runs.

**TABLE 4: Reuse of the CMZO for the synthesis of 3c (TABLE 1)**

<table>
<thead>
<tr>
<th>Yield (%)</th>
<th>Time (min)</th>
<th>Run</th>
</tr>
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<tbody>
<tr>
<td>95</td>
<td>25</td>
<td>first</td>
</tr>
<tr>
<td>95</td>
<td>25</td>
<td>second</td>
</tr>
<tr>
<td>94</td>
<td>30</td>
<td>third</td>
</tr>
</tbody>
</table>

Refers to the isolated yields

**CONCLUSION**

In summery, we have developed a simple, efficient and clean procedure for the synthesis of 5-arylidinemalononitrile derivatives by condensation of various aromatic aldehydes and malononitrile in the presence of CMZO solid heterogeneous catalyst. Also in the present method ethanol:water \((1:1)\) is used as a solvent and therefore which is relatively eco-friendly and supporting to green chemistry. In addition to that, the present method offers some advantages in terms of simplicity of performance, easy work-up, use of inexpensive, easy to handle and eco-friendly catalyst, high yields of products and relatively short reaction times.

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