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Highly Efficient Cerium Metal Organic Frameworks (Ce-Uio-66) and Its Inorganic Hybrids Nanocomposite as Novel Heterogenous Catalyst for Knoevenagel Condensation Reaction

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ABSTRACT

Heterogeneous catalysis is a prominent application of metal-organic frameworks (MOFs), which have garnered significant interest from researchers over the past two decades due to their unique hybrid organic/inorganic nature. This study aimed to synthesize Ce-UiO-66 and its inorganic hybrids (Cds/CeUiO-66/Ag_3PO_4) and to assess their effectiveness as heterogeneous catalysts in the Knoevenagel condensation reaction. All materials were synthesized through hydrothermal methods and characterized using X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The organic components were analysed with 1H-NMR and 13C-NMR spectroscopy. The catalytic performance of Ce-UiO-66 and its inorganic hybrids was evaluated under optimized conditions for various aldehyde substrates and malononitrile in aqueous media, focusing on reaction time, catalytic activity, and yield. The results showed that the yield of the target product followed this trend: T1 > Cds/Ce-UiO-66 > Ce-UiO-66. The catalytic system was also tested with various aromatic aldehydes, achieving over 90% conversion at room temperature. Additionally, the catalyst maintained its catalytic efficiency after being reused more than three times. Overall, this research highlights the synthesis of Ce-MOF and its inorganic hybrids and their catalytic performance in the Knoevenagel condensation reaction.

Keywords: Heterogeneous Catalysis, Inorganic Hybrids (Cds/Ce-UiO-66/Ag_3PO_4), Knoevenagel Condensation, Cerium Metal Organic Frameworks (Ce-UiO-66)

Introduction

Given the environmental and economic concerns, heterogeneous catalysis stands out as a highly impactful industrial application. While the exceptional intrinsic properties of microporous heterogeneous catalysts are essential, they are not sufficient for their successful industrial adoption [1]. The primary objective of heterogeneous catalysis is to design and synthesize catalysts with specific active sites to attain the desired activity and selectivity, rooted in a molecular-level understanding of the underlying mechanisms. The creation of highly active and selective catalysts is particularly important for advancing green chemistry [2]. Therefore, exploring well-defined metal-organic frameworks (MOFs) and their hybrids with varying sizes and compositions is integral to achieving this goal.

MOFs are a class of porous materials formed through strong bonds between metal ions and organic linkers. These versatile materials are applicable across various fields, but their role in catalysis has drawn significant interest [3]. MOFs have been utilized as solid catalysts and catalyst supports for diverse organic transformations [4-5].

Among these transformations, the Knoevenagel condensation reaction has garnered considerable attention due to its utility in organic chemistry, particularly for forming carbon-carbon bonds through the reaction of carbonyl compounds with active methylene compounds. Recently, there has been an increasing interest in the products of Knoevenagel condensation, as many

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exhibit notable biological activity and are valuable in fine chemicals and therapeutic products [6].

Scheme 1: Schematic representation of Knoevenagel condensation

A range of homogeneous and heterogeneous catalysts have been explored for the Knoevenagel condensation, including ammonia, primary and secondary amines, pyridine, NAP-SiO2, hydroxyapatite, lithium hydroxide, ionic liquids, organ catalysts like DABCO, MgBr2.OEt2, and nano-MgO/Bulk-MgCl2 [7-15]. However, these methods often face challenges such as low yields, prolonged reaction times, excessive catalyst amounts, harsh reaction conditions, usage of hazardous solvents, non-recoverable toxic metal-containing catalysts, moisture sensitivity, and complicated work-up procedures [16]. Hence, there is a pressing need to devise a more efficient approach that circumvents these issues.

In this study, we present a greener methodology for synthesizing Knoevenagel condensation products using a highly efficient, reusable, and environmentally friendly heterogeneous nano-catalyst that achieves good to excellent yields in shorter reaction times. We report the synthesis of Ce-UiO-66 and its inorganic hybrids, specifically Cds/Ce-UiO-66/Ag_3PO_4, using various ratios of Cds to Ce-UiO-66/Ag_3PO_4 (1:1, 0.75:1, and 0.5:1) within the MOF composites. The catalytic performance of these materials is evaluated in the Knoevenagel condensation of benzaldehyde and malononitrile under optimized room temperature conditions, with the catalyst achieving the highest yield undergoing further testing with different aldehyde substrates.

Experimental Procedures

Chemicals and Reagents

All reagents and chemicals utilized were of reagent grade or higher quality and were used directly without any additional purification steps.

Preparation of Nano catalysts

Synthesis of Ce-UiO-66

The synthesis of Ce-UiO-66 was conducted following the method described in, with minor modifications [17]. Specifically, 4.3445 g (11.62 mmol) of cerium nitrate hexahydrate (Ce (NO3)3·$8H_2O$) and 2.4803 g (14.92 mmol) of terephthalic acid (TPA) were each dissolved in 50 mL of deionized water (DIW). An equimolar (1 M) ammonia solution was then incrementally added to the linker solution to completely deprotonate the organic acid while maintaining pH control. Subsequently, the metal salt solution was mixed into the linker solution under magnetic stirring for 1 hour. The resulting white precipitate was centrifuged at 2500 rpm for 20 minutes, washed three times with DIW and ethanol, and filtered. The final white solid was dried in an oven at 60 °C for 24 hours and labelled as S1.

Synthesis of Cds/Ce-UiO-66

The Cds/Ce-UiO-66 composites were synthesized using a modified method similar to that for pure Cds. A total of 1.00 g each of UiO-66 and Cd $(CH_3COO)_2\cdot 2H_2O$ were dispersed in 50 mL of DIW, which was then placed in an oven and heated at 100 °C for 12 hours. Following cooling to room temperature, the precipitates were collected via centrifugation and purified several times with DIW and ethanol. The final products were dried at 60 °C under vacuum and designated as Cds/UiO-66, referred to as B1 [18,19].

Synthesis of Ce-UiO-66/Ag_3PO_4

UiO-66 (Ce)/Ag_3PO_4 composites were synthesized using an in-situ ion-exchange precipitation method, involving the direct substitution of cerium into Zr-MOF [20]. Initially, 1.01 g of the as-prepared Ce-UiO-66 was dispersed in 100.0 mL of distilled water and sonicated for 30 minutes. Next, 1.0 g of AgNO3 was added and sonicated for an additional 30 minutes. Subsequently, 0.7 g of $Na_2HPO_4\cdot 12H_2O$ was dissolved in 10.0 mL of distilled water and added dropwise to the mixture under vigorous stirring. After 12 hours of stirring, the final products were collected by filtration, washed three times with distilled water and ethanol, and dried in an oven at 60 °C for 2 hours, labelled as B2.

Synthesis of Ternary Cds/UiO-66-Ce/Ag_3PO_4

The ternary nanocomposite Cds/UiO-66-Ce/Ag_3PO_4 was prepared by combining 1.0 g of the UiO-66-Ce/Ag_3PO_4 nanocomposite with three different molar ratios of Cds relative to the UiO-66-Ce/Ag_3PO_4, specifically 1:1, 0.75:1, and 0.5:1. The binary composite was dissolved in 50 mL of deionized water and sonicated for 2 hours, followed by the addition of a calculated amount of $Cd(CH_3COO)2$, which was sonicated for an additional 30 minutes. Next, a stoichiometric amount of $Na_2S\cdot 9H_2O$ was dissolved in 50 mL of deionized water and added to the mixture, which was stirred vigorously for 12 hours. The resulting blue-black precipitate was collected, washed three times with deionized water and ethanol, and dried in an oven at 80 °C for 6 hours.

Characterization of Synthesized Ce-UiO-66 and Its Inorganic Hybrid Catalysts

The synthesized nano catalysts were characterized using X-ray diffraction (XRD) with a Philips X'PERT Pro Analytical diffractometer equipped with an X'Celerator detector. Cu Kα radiation (λ = 1.5418 Å) was employed to ascertain crystalline structure and phase purity, with crystal size calculated using the Scherer equation. Diffraction patterns were collected at 2θ values ranging from 5 to 70 degrees.

Scanning electron microscopy (SEM) was utilized to analyze the morphology and particle distribution of the obtained nano catalysts using a Hitachi TM1000, complemented by energy-dispersive X-ray spectroscopy (EDX) for elemental analysis. The elemental weight percentage of the synthesized sample was determined through EDX, with a 40-second acquisition time, 3-hour processing duration, and an accelerating voltage of 15 kV. High-resolution transmission electron microscopy (HRTEM) images were captured with a JEOL 2100F electron microscope operating at 200 kV, equipped with an INCA x-sight detector from Oxford Instruments.

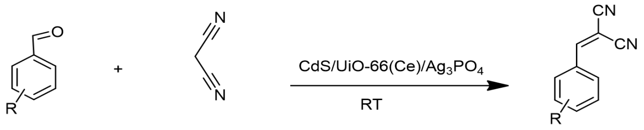
Optimization of Reaction Conditions

The optimization study focused on the Knoevenagel condensation reaction, specifically the reaction between benzaldehyde and malononitrile, as a model for the Knoevenagel condensation. The parameters optimized included temperature, solvents, and catalyst loading of the prepared nanomaterials.

Evaluation of Catalytic Activity

General Procedure for the Knoevenagel Condensation

The catalytic activity was evaluated following the method previously described in [21]. The Knoevenagel condensation of benzaldehyde with malononitrile took place in a three-necked round-bottom flask equipped with a magnetic stirrer. In a typical reaction setup, a mixture comprising 0.28 g (2.5 mmol) of benzaldehyde and 0.132 g (2 mmol) of malononitrile (in a benzaldehyde/malononitrile ratio of 2.5:2 mol/mol) was prepared. The synthesis of the catalyst was adjusted by varying its concentration in increments of 5 mg, starting from 5 mg, to determine the optimal catalyst loading under solvent-free conditions. At various time intervals, aliquots of the reaction mixture were withdrawn, and after separating the catalysts by centrifugation, the progress of the reaction was monitored using thin-layer chromatography (TLC).



Scheme 2: The Knoevenagel Condensation of Benzaldehyde with Malononitrile

Results and Discussion

Catalyst Synthesis and Characterization

In this study, Cds, Ag_3PO_4, Ce-MOF, and their inorganic hybrids (Cds/UiO-66-Ce, UiO-66-Ce/Ag_3PO_4, and Cds/UiO-66-Ce/Ag_3PO_4) with various molar ratios (1:1, 0.75:1, and 0.5:1 of Cds to UiO-66/Ag_3PO_4) were synthesized using precipitation and hydrothermal methods. The resulting materials were characterized using a range of analytical techniques.

XRD Analysis

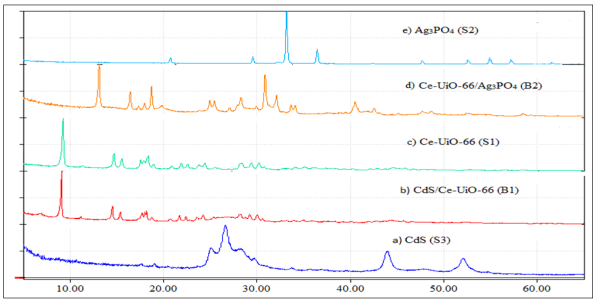


Figure 1: XRD Spectra of Ce-UiO-66, Cds, Ag_3PO_4, Cds/Ce-UiO-66, and Ce-UiO-66/Ag_3PO_4

The XRD pattern of Cds is presented in Figure 1a, showcasing three distinct diffraction peaks at 2θ values of 26.67°, 44.00°, and 52.05°, corresponding to the Miller indices (100), (202), and (311), indicative of the hawleyite structure of Cds [96-101-1261]. These findings align with the previously published literature [19]. The XRD pattern of Ag_3PO_4, displayed in Figure 1e, reveals major peaks around 2θ = 20.9°, 29.7°, 32.3°, 33.3°, 36.6°, 38.1°, and 42.5°, confirming the presence of a cubic structure of Ag_3PO_4, with no impurity peaks noted, suggesting high purity and good crystallization of the microcrystals [12, 22, 23].

As illustrated in Figure 1c, the main diffraction peaks for the MOFs are located below a scattering angle (2θ) of 10°, characterizing them as porous materials with abundant cavities. A decrease in 2θ values corresponds to an increase in porosity and MOF-like characteristics [24]. The significant peaks in the XRD patterns of UiO-66 (Ce-MOF) are consistent with those reported in the literature, while peaks at 28.2°, 29°, 46.7°, and 48.7° indicate the presence of CeO_2 [25-27].

Figure 1b shows the XRD patterns for Cds/Ce-UiO-66, where peaks related to both materials are visible. However, the prominent peak at 2θ = 26.67° corresponding to Cds appears diminished, likely due to the dispersion of these crystals within the MOF structure. Similarly, the Ce-UiO-66/Ag_3PO_4 nanocomposite depicted in Figure 1d also exhibits peaks associated with both components, although a notable shift in peak positions is observed compared to the Cds/Ce-UiO-66 composite.

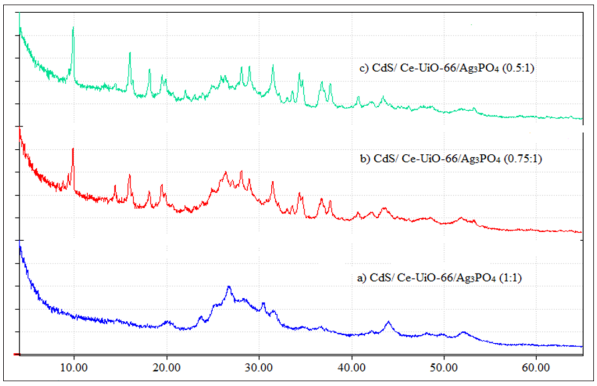


Figure 2: XRD Spectra of Three Different Molar Ratios of Cd:Ce in Cds/Ce-UiO-66/Ag_3PO_4 (1:1 (T1), 0.75:1 (T2), and 0.5:1 (T3))

In the ternary systems, it was noted that the amount of Cds significantly impacted the MOF structure. At a Cds to Ce-UiO-66/Ag_3PO_4 ratio of 1:1, the MOF structure was compromised, resulting in a more amorphous material resembling Cds than a composite. Consequently, no diffraction peak attributable to Ag_3PO_4 was detected. In the other compositions, the MOF structure remained intact, and peaks related to Ce-UiO-66, Ag_3PO_4, and Cds were all evident.

The average crystallite size of the as-synthesized UiO-66(Ce-MOF) can be calculated using the Debye Scherrer formula;

$$Ds = 0.9\,\lambda / \beta Cos\theta \tag{1}$$

Where Ds = is the average crystallite size; λ= is the wavelength of the X-rays equals to 0.15406 nm corresponds to the Cu target Kα radiation; β = is the full width of half-maximum (FWHW) of an XRD, and θ = is the Bragg diffraction angle in radians.

Table 1: Average crystallite sizes of the as-synthesized nanomaterials

Sample	2θ (degree)	β (radians)	Ds (nm)
Ce-UiO-66	9.3	0.0035	39.6
Cds	26.48	0.0140	10.3
Ag_3PO_4	33.31	0.0035	40.8
Cds/Ce-UiO-66	9.03	0.0023	60.3
Ce-UiO-66/Ag_3PO_4	13.11	0.0035	39.6
Cds/Ce-UiO-66/ Ag_3PO_4 (1:1) (T1)	26.62	0.0257	5.5
Cds/Ce-UiO-66/ Ag_3PO_4 (0.75:1) (T2)	26.22	0.0245	5.8
Cds/Ce-UiO-66/ Ag_3PO_4 (0.5:1) (T3)	9.86	0.0023	60.3

All the as-synthesized materials fall in the nanoscale.

SEM-EDX Analysis

The morphologies and elemental compositions of the synthesized Ce-UiO-66 and its inorganic hybrids (Cds/Ce-UiO-66, Ce-UiO-66/Ag_3PO_4, and Cds/Ce-UiO-66/Ag_3PO_4 in varying proportions) were examined using SEM-EDX (see Figures 3a-h).

The SEM images of the Ce-UiO-66 products displayed rice-like crystals with an average width of approximately 100 nm (Figure 3a). Additionally, numerous small microcrystals with an average edge length of around 300 nm exhibited a uniform size distribution. Figure 3b illustrates that the Ag3PO4 has a consistent cubic shape and even distribution. The SEM image of Cds (Figure 3c) shows well-defined crystalline grains, with a close examination revealing a hexagonal structure characteristic of greenockite-like nanoparticles. The EDX spectra for each phase confirm the presence of specific elements: only cerium for Ce-UiO-66, silver and phosphorus for Ag_3PO_4, and cadmium and sulfur for Cds nanoparticles, thus confirming the formation of pure phases without impurities. For instance, the elemental ratio of Cd to S was found to be 81.4% to 18.6%, indicating nearly complete consumption of the cadmium precursor used, which aligns well with previously reported results [28].

In the binary system of Cds/Ce-UiO-66, the SEM image clearly displays the pore structure of the MOFs with Cds crystals deposited on them (Figure 3d). In contrast, the binary system Ag_3PO_4/Ce-UiO-66 (Figure 3e) reveals a distinct rice-like structure of the MOF interspersed with Ag_3PO_4 crystals. The EDX spectra for both cases confirm the presence of all components, validating the purity of the phases, although the latter exhibits some heterogeneity (Figure 3e).

In the ternary systems (Figures 3f-h), the unique morphologies observed in the individual phases disappear upon composite formation, indicating a thorough mixing of components. The EDX spectra in all instances confirm the presence of each component within the ternary system.

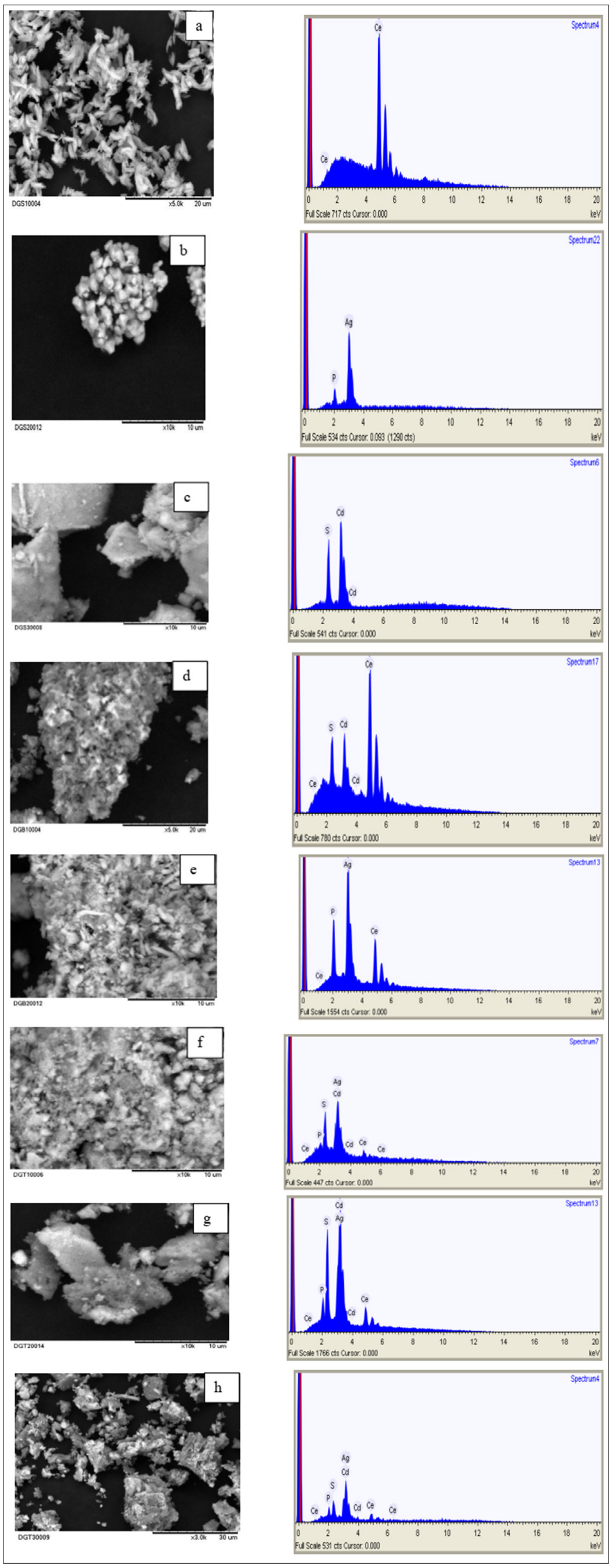


Figure 3: SEM micrograph of a) S1; b) S2 C) S3 d) B1 e) B2 f) T1 g) T2 h) T3 at high magnification and corresponding EDX spectra

Evaluation of Catalytic Studies

Catalyst Selection for Knoevenagel Condensation

To evaluate the catalytic performance of Ce-UiO-66 and its inorganic hybrids, we conducted a model reaction using benzaldehyde and malononitrile to synthesize 2-benzylidenemalononitrile through the condensation of various benzaldehyde substrates with malononitrile (see Scheme 2). Initial trials utilized 100 mg of the synthesized ternary nanocomposites at different molar ratios to identify the most effective catalyst for achieving a high percentage yield in the model reaction. The catalyst with a 0.5:1 ratio (Cds/Ce-UiO-66/Ag_3PO_4) demonstrated the highest yield at 65%, outperforming the 1:1 and 0.75:1 ratio, which yielded 62% and 57%, respectively, within a 20-minute reaction timeframe (refer to Table 3). Notably, we observed a 20% yield of product in the absence of a catalyst at room temperature over 12 hours (Table 3, entry 1). Consequently, the Cds/Ce-UiO-66/Ag_3PO_4 catalyst was chosen for further optimization, as indicated in Table 3. Upon optimizing the catalyst quantity, we determined that 10 mg of the 0.5:1 molar ratio of Cds/Ce-UiO-66/Ag_3PO_4 efficiently catalysed the synthesis of the desired product.

Table 3: Catalyst Selection for Knoevenagel Condensation

Catalyst	Time (Min)	Yield (%) a
Ce-UiO-66	120	64
Cds	140	48
Ag_3PO_4	115	37
B1	170	60
B2	167	55
T1	150	57
T2	143	62
T3	120	65

a) Reaction conditions: 2.5 mmol of benzaldehyde, 2 mmol of malononitrile, 100 mg of catalyst, 5 ml of solvent. Key: B = binary nanocomposite, T = ternary nanocomposite.

From table 3 the catalyst 0.5:1 ratio (Cds/Ce-UiO-66/Ag_3PO_4) affords better yield (65%) when water was used as a solvent and the reaction proceeded at room temperature as compared to the rest of the as-synthesized catalyst within 120 min reaction time. The high activity of the Cds/CeUiO-66/Ag_3PO_4 catalyst is attributed to the better stability of this MOF compared with Ag_3PO_4/Ce-UiO-66. Not only this, the SEM micrographs showed poor mixing of the Ag_3PO_4 particles with the MOFs in B2. The silver phosphate particles being quite distinct on the surface make them exposed to the solution. This reduces their stability compared to the case in which the particles grow inside the MOF structure. We noted poor porosity on SEM image of this binary composite. Therefore, the catalyst with 0.5:1 ratio (Cds/Ce-UiO-66/Ag_3PO_4) was selected for the optimization process.

Optimization of Solvent

The reaction was conducted using three different solvents, with water proving to deliver satisfactory yields of the desired product. Given its environmental benefits, water serves as a cleaner and more economical solvent option. To minimize environmental impact, organic reactions should favour water over volatile solvents. Conducted at room temperature, the reaction produced a suitable yield of the analogous product (see Table 4, entry 1). Notably, the reaction was observed to be slowest in less polar solvents. Thus, water emerges as the optimal solvent due to its high yield and shorter reaction time compared to the alternatives.

Table 4: Optimization of solvent for Knoevenagel condensation

Entry	Solvent	Time (Min)	Yield (%)a
1	H_2O	120	65
2	DMF	140	52
3	Toluene	145	55

a) Reaction conditions: 2.5 mmol benzaldehyde, 2 mmol malononitrile, 100 mg of catalyst, and 5 mL of solvent.

Optimization of Reaction Temperature

The impact of temperature on the reaction was assessed by performing experiments at various temperatures: room temperature (25 ºC), 50 ºC, and 75 ºC, using 100 mg of catalyst. As indicated in Table 4, increasing the temperature from room temperature to 50 ºC and then to 75 ºC resulted in decreasing yields. Therefore, it can be concluded that 25 ºC is the most effective temperature for these reactions.

Table 5: Optimization of reaction temperature for Knoevenagel condensation

Temperature (°C)	Time (Min)	Yield (%) a
RT	120	65
50	140	59
75	135	55

a) Reaction conditions: 2.5 mmol benzaldehyde, 2 mmol malononitrile, 5 mL water, 100 mg catalyst. Optimization of Catalyst Load.

A preliminary control experiment was conducted to assess the reaction rate without the catalyst, which yielded only 40.9% of 2-benzylidenemalononitrile after 720 minutes (see Table 3, entry 1). Increasing the load of the Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1) nano catalyst resulted in a notable enhancement in conversion rates, with yields rising from 55.65% to 88.0%. However, no significant yield improvement was observed between entries 4 and 5 in Table 6, indicating that the catalyst amount in entry 4 represents the optimal balance between catalyst quantity and reaction duration.

Table 6: Optimization of Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1) ratio of Cd:Ce in the reaction of benzaldehyde and malononitrile based on catalyst concentration, reaction time, and yield.

Entry	Catalyst load (mg)	Time (Min)	Yield (%) a
1	blank	720	40.9
2	Cds/Ce-UiO-66/Ag_3PO_4 (5)	120	55.65
3	Cds/Ce-UiO-66/Ag_3PO_4 (10)	20	88.0
4	Cds/Ce-UiO-66/Ag_3PO_4 (15)	28	77.02
5	Cds/Ce-UiO-66/Ag_3PO_4 (20)	30	68.4

a) Reaction conditions: 2.5 mmol benzaldehyde, 2 mmol malononitrile, 5 mL solvent (H_2O), and room temperature.

Application of the Optimized Reaction Conditions for Various substituted aldehydes

With these results in hand, we obviously explore the potential of this catalyst further by examining the Knoevenagel condensation between different substituted aldehydes and malononitrile under the optimized conditions. When the catalyst (Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1)) was applied to a mixture of various substituted aldehyde and malononitrile water, complete disappearance of the starting aldehyde occurred at 20 min and the 1H- NMR analysis showed the presence of sole product of the reaction (entry 1).

Various substituted aldehydes were applied as reactants to study the catalytic efficiency (Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1)). The corresponding results revealed that the catalyst (Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1)) produced yield (88 %, entry 1) when the substrate is benzaldehyde and same amount (88 %, entry 2) of the yield was obtained with reactants having for the withdrawing groups -NO2 group. However, the reaction yields of aldehydes with electron donor groups (two -OMe groups, entry 5 and amine group entry 4) reduced to 83 and 78, respectively as noted in the above Table 7. Furthermore, for bulky functional groups like electron donor groups (two -OMe groups, entry 5) reduced to 78 % as noted in the above Table 7 and this may be caused due to the steric hindrance since the reaction takes place inside the pore of the material. Altogether, the small differences in the surface density of basic sites (ρ) indicate that both Lewis acid sites and basic sites, i.e. the "M+n–O2 Lewis acid–base" pair, act more efficiently in the conversion [21]. Generally, the presence of a substituent on benzaldehyde such as electron withdrawing or electron donating group can produce a deep effect on the product yield in the Knoevenagel condensation reaction with no specific trend [29].

Table 7: Knoevenagel condensation reactions of different aldehyde substrates using Cds/Ce-UiO-66/Ag_3PO_4

Entry	Aldehyde Substrate	Yield (%) a
1	Benzaldehyde	88
2	Substituted Aldehyde (-NO2)	88
3	Substituted Aldehyde (Amine)	78
4	Substituted Aldehyde (-OMe)	83
5	Bulky Aldehyde (-OMe, -OMe)	78

(a) Reaction conditions: 2.5 mmol aldehyde substrate, 2 mmol malononitrile, 10 mg Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1) catalyst, 5 mL H_2O at room temperature

Comparison of Different Catalysts for the Knoevenagel Condensation Reaction

Comparing our catalyst's performance with existing options, UiO-66-NH_2 has been documented as a heterogeneous catalyst for the Knoevenagel condensation of benzaldehyde with either ethyl cyanoacetate or malononitrile [30]. Specifically, UiO-66-NH_2 achieved a 94% conversion for benzaldehyde with ethyl cyanoacetate in ethanol at 80 °C, and a conversion rate of 98% at 40 °C for the reaction between benzaldehyde and malononitrile, yielding results in significantly shorter time spans. This enhanced catalytic activity could be attributed to numerous factors inherent to its structural properties. On the other hand, the reaction between benzaldehyde and malononitrile using UiO-66-NH_2 afforded 98 % conversion at 40 °C in much shorter time. This high catalytic conversion of Knoevenagel condensation may be due to the presence of amine group on the MOF which is responsible for basic sites to facilitate the reaction.

In another work, UiO-66-NH-RNH2, MIL-101(Cr)-NH-RNH_2 and MIL-53(Al)-NH-RNH_2 samples were evaluated as catalysts in the Knoevenagel condensation between benzaldehyde and malononitrile [31]. It was observed that UiO-66-NH-RNH_2 and MIL- 101(Cr)-NH-RNH_2 catalysts gave 97 and 99 % yields, respectively, towards the expected condensation product at room temperature. Besides this, MIL-53(Al)-NH-NH_2 also gave 87% yield for this reaction under identical conditions.

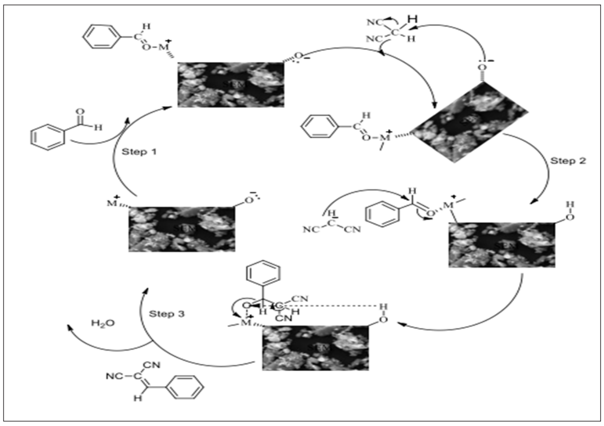
Proposed mechanism for Knoevenagel condensation.

Knoevenagel condensation reactions can be catalysed by bases, acids or materials containing both acidic and basic sites. The possible mechanism for Knoevenagel condensation of benzaldehyde with malononitrile catalysed by Cds/Ce-UiO-66/Ag_3PO_4 could be described based on previous report as follows [32].

Step 1: The activation of the carbonyl group of benzaldehyde proceeds at the Lewis acid site. At the same time, the detachment of an acidic proton of the methylene group of malononitrile, giving a carbonium anion, occurs at the basic site of the MOF.

Step 2: The carbonium anion reacts with the carbonyl group of benzaldehyde to give intermediate (I),

Step 3: Further desorption of the Knoevenagel reaction product followed by release of the water molecule results in complete regeneration of the catalyst active site.



Scheme 2: Proposed mechanism for the synthesis of Benzylidene malononitrile

Characterization of the Synthesized Organic Product

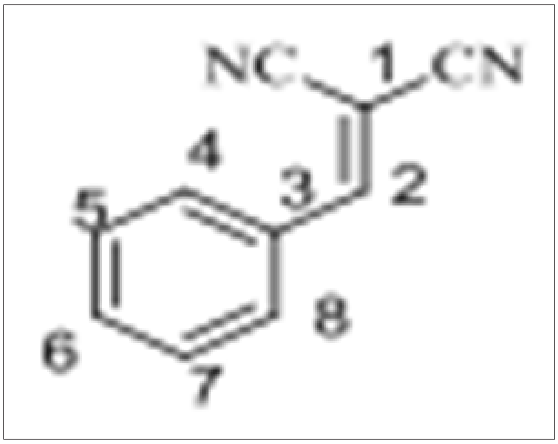
The conversion rate and purity of the organic compounds were assessed using thin-layer chromatography (TLC) and measured melting and boiling points. In addition to TLC and melting point analysis, some synthesized organic compounds were structurally characterized and evaluated for purity through spectroscopic techniques, such as 1H NMR, 13C NMR, and DEPT-135 spectra, utilizing DMSO d6 as the solvent.

Table 8: presents the chemical shift values from the 1H-NMR spectrum for 2-benzylidinemalononitrile in DMSO

1H-NMR Type	Chemical Shift Value
-CH(CN)2	8.4-8.6
-CH (Aromatic at C-4 and C-8)	7.9-8.0
-CH (Aromatic at C-5, C-6, and C-7)	7.6-7.7

Table 9: The carbon position data from the 13C-NMR spectrum (δ ppm) are as follows:

Carbon Position	13C-NMR δ (ppm)	Remark
2	162	
3	134	
4, 5, 6, 7, 8	129-131	
	113-114	
1	82	=CH
		=CH-(aromatic ring)
		=CH-(aromatic ring)
		nitrile group (-CN)
		-HC=C(CN)2



Scheme 3: Structure of 2-benzylidinemalononitrile

Catalytic Reusability of the Synthesized Nano catalyst

The reusability of the Ce-based organic framework and its inorganic hybrids was investigated in the Knoevenagel condensation of benzaldehyde (BA) and malononitrile (MN) over three consecutive runs under consistent experimental conditions. After each reaction, the Ce-based framework and its hybrids were isolated via suction filtration, thoroughly washed with ethanol, and outgassed in an oven at 100 °C for 24 hours. The recovered catalyst was reused in a new catalytic reaction under identical conditions, with progress monitored by TLC.

The graph illustrates that the recycling process did not lead to a significant reduction in catalytic activity, maintaining approximately 78% of the initial benzylidene malononitrile yield even after three cycles. These results indicate that the catalytic efficiency of the ternary nanocomposite remains largely unaffected over multiple catalytic runs.

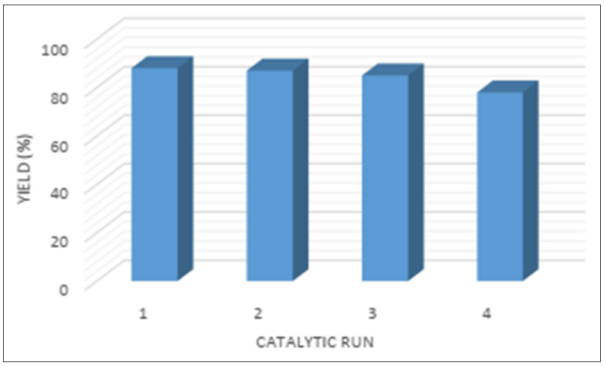


Figure 5: Reusability of Cds/Ce-UiO-66/Ag_3PO_4 in the Knoevenagel Condensation of Benzaldehyde and Malononitrile.

Conclusions

In this study, Ce-UiO-66, Cds, Ag_3PO_4, and their inorganic hybrids were successfully synthesized using co-precipitation and a simple hydrothermal method at room temperature. This method is advantageous as it avoids the use of organic solvents and operates at 25 ºC, adhering to Green Chemistry principles. The synthesized materials were characterized using PXRD and SEM-EDX, confirming that all compounds, including the Ce-UiO-66, Cds, Ag_3PO_4, and their hybrids, were crystalline and aligned with previously reported data. XRD results indicated that both Cds/Ce-UiO-66/Ag_3PO_4 (1:1 and 0.75:1) and Cds exhibited smaller crystalline sizes, placing them in the nanoscale range. SEM images revealed rice-like particles for Ce-UiO-66 and cubic structures for Cds.

These synthesized materials serve as heterogeneous catalysts for the Knoevenagel condensation of various benzaldehyde substrates with malononitrile, demonstrating a catalytic efficiency yield of 88% for the ternary composite of Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1). The yield remained consistent for both benzaldehyde and substrates with electron-withdrawing groups. During the reusability tests, the Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1) catalyst was successfully separated by suction filtration and could be recovered and reused without significant loss of catalytic activity over three consecutive runs. Thus, the synthesized Cds/Ce-UiO-66/Ag_3PO_4 (0.5:1) is a viable heterogeneous catalyst for the Knoevenagel condensation reaction.

Disclaimer (Artificial Intelligence)

Author(s) hereby declares that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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