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Synthesis and characterization of nano $CuO/ZnO/Al_2O_3$ catalyst via Laser ablation route for the preparation of some cyanoacetanilide derivatives

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Abstract

The laser ablation technique can be considered as a promising and effective physical alternative route that may be used for the creation of nanoparticles. The main goal of this study is to synthesize$CuO/ZnO/Al_2O_3$glass-ceramic nanoparticles in aqueous media using the laser ablation route in deionized water (DIW). Synthesized nanoparticles were employed for the synthesis of 2-cyano-2-(p - nitrobenzylidene)- p -methoxyacetanilide via Knoevenagel condensation reaction between p-nitrobenzaldehyde and 2-cyano-N-(4methoxyphenyl) acetamide compounds. This protocol was used to obtain a high yield of the final product. The method is considered solvent-free, eco-friendly, short-time reaction, and excellent yield in comparison with that using the catalyst in its bulk form. The antibacterial properties of the synthesized products were evaluated against Gram-positive (*Streptococcus bacteria*) and Gram-negative bacteria (*Enterococcus bacteria*).

Keywords: Nanomaterial; $CuO/ZnO/Al_2O_3$; Cyanoacetanilide; Laser ablation

1. Introduction

Industrial and academic communities have investigated commercial applications of transition metal oxide nanoparticle catalysts in the production of critical chemical intermediates. Metal oxide nanoparticles have a high selectivity in catalysis, which allows them to differentiate between chemical groups, resulting in high yields of the anticipated product [1]. Because of their diverse structures, porosity, and high surface area, metal-organic frameworks (MOFs) are promising candidates for the immobilization of guest active species in recent decades. This study successfully synthesized silicotungstic acid (HSiW) encapsulated UiO-66 using a one-pot synthesis strategy, A single factor experimental technique combined with response surface methodology (RSM) was used to investigate the influence of esterification process parameters on biodiesel production; a high conversion of 80.5 percent was attained using single factor optimization and 92.8 % using RSM. More importantly, when the catalysts wereused six times, the conversion of lauric acid dropped from 80.5 percent to 70.2 percent [2]. Structural, spectroscopic, and physical character variations of specific nanocatalyst wereadopted for different condensation reactions to produce imidazole derivatives with high yields and short reaction times at room [3]. Magnetic nanocatalystsalso are considered a new and promising field of study that may be used in the synthesis of complex products from simple starting materials [4]. Nanoalloys (NAs), which differ from bulk alloys or single metals, have inherent properties such as tuneable components and other materials for catalytic performance optimization. Furthermore, the correlations between composition/structure and catalytic properties are discussed [5].Bis[(3-aminopropyl) triethoxysilane]dichloride was prepared and immobilized on magnetic nano—$Fe_2O_3@SiO_2$. Following the reagent's characterization, it was utilized to efficiently enhance the Knoevenagel reaction, resulting in high reaction rates and yields. In addition, the catalyst's recovery and reusability of the investigated reaction were good [6]. A Co/Al layered double hydroxide material was produced in both bulk and exfoliated (colloidal) forms. Anion exchange with methionine enabled the immobilization of Au nanoparticles that had previously been prepared using a biomimetic method that used an anti-oxidant tea aqueous extract

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to reduce the Au salt solution. In aerobic olefin epoxidation, the catalytic performance of bulk and exfoliated clay Au-hybrid materials was evaluated. After 80 hours of reaction time, both catalysts were very active toward epoxide products and had very interesting substrate conversion levels [7, 8]. A standard meltquenching method was used to make the $CuO/ZnO/Al_2O_3$ glass-ceramic. In the presence of $CuO/ZnO/Al_2O_3$ catalyst, the generated catalyst was used for a Knoevenagel-type reaction under solvent-free conditions via an efficient one-pot multicomponent reaction of 2-cyano-p-methoxyacetanilide and p-nitrobenzaldehyde. In comparison to that previously synthesized using piperidine, the generated acetanilide derivative was discovered to be adequately synthesized withoutstanding yields in the presence of $CuO/ZnO/Al_2O_3$ catalyst [9-11]. Researchers also confirmed their results using a density functional theory (DFT)-based energy gap computed from HUMO-LUMO calculations [12].Many of such products were tested for their antibacterial activity against *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) bacterial strains and were determined using gruesome assays. Both incorporated mixtures were tested in vitro for antibacterial activity against *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) bacterial strains, as well as the standard anti-infection medication gentamicin [13]. This study shows how to upgrade receptive dye and functional completing of fleece yarns by simply joining them together with integrated chitosan-acrylamide half and half. Fourier transforms infrared spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques were used to combine and depict this. It was then attached to fleece, portrayed with FTIR, SEM, and weight acquisition tests, as well as dye capacity with two business-sensitive colors. The results showed that Ch-Ac treated fleece could be colored faster (30 minutes) and with a higher degree of receptive color (2 percent) than untreated fleece. More extreme colors, not possible with regular coloring, could be achieved using Ch-Ac treated fleece. Furthermore, Ch-Ac treatment-induced extreme searching and antibacterial activity in both gram-negative (E. coli) and gram-positive (S. aureus) bacteria [14-16].

The main aim of the represented work is to introduce a new technique for the synthesis of ($CuO/ZnO/Al_2O_3$) glass-ceramic nanocatalyst through the laser ablation route and to use such a catalyst for the synthesis of some cyanoacetanilide compounds with high yield products and reusable for several times. The synthesized products were tested against different pathogenic grams to examine their activities

2. Experimental

2.1 **Materials and Methods**

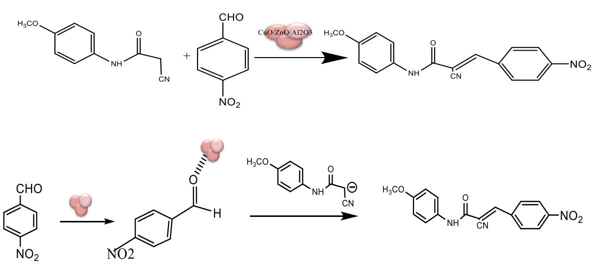
All chemicals used during the study are of analytical grade, supplied by Sigma-Aldrich co and used as received without further purification. Melting points were determined in degrees Celsius using the Gallenkamp electric melting point instrument. Functional group vibrations were examined using the ordinary FTIR using the KBr disc route, recorded on the transmission mode via Thermo Scientific Nicolet iS10 FTIR single beam spectrometer. UV/Visible spectra were analyzed using a double beam spectrophotometer pg T180. Powdered X-ray diffraction (XRD) was recorded via PANalyticalX'Pert PRO diffractometer adopting mono-chromatized Copper, potassium α radiation (λ =1.5406 Å) operated with 45kV-40mA within Bragg angle between 5-80°. The composition of the studied sample was estimated for a powdered sample using a portable X-ray Fluorescent (XRF) X-MET 8000 ideal, oxford instrument.

2.2 Preparation and characterization of $CuO/ZnO/Al_2O_3$ nanoparticles.

A bulk sample of $CuO/ZnO/Al_2O_3$ was previously prepared and studied using an ordinary melt quenching route and reported by Abdelghany et al [16]. The laser ablation technique in water was carried out at 355nm as an eco-friendly technique for the generation of catalyst nanoparticles with spherical shape in the range of 20-50 nm diameter as previously reported for different materials [17, 18].

2.3Preparation of 2-cyano-2-(p - nitrobenzylidene)- p -methoxyacetanilide).

0.57g of 2-cyano-*N*-(4-methoxyphenyl) acetamide in 40 mL of ethanol was added to 0.453 g of *p*-nitrobenzaldehyde was added. 0.01 g of catalyst $CuO/ZnO/Al_2O_3$ and reaction components were refluxed for about 1 hour. The product (2-cyano-2-(p - nitrobenzylidene)- p -methoxyacetanilide) Scheme 1. was collected and purified by recrystallization (M.B =210 °C) and then the product was characterized through FT-IR, ^{13}C-NMR, and ^{1}H-NMR spectroscopic techniques.



$CuO/ZnO/Al_2O_3$ catalyst

Scheme 1. Preparation of 2-cyano-2-(p - nitrobenzylidene)- p -methoxyacetanilide by Knoevenagel condensation reaction

3. Result and discussion

3.1. ***$CuO/ZnO/Al_2O_3$nanocatalyst structural characterization***

Figure 1 depicts the X-ray diffraction pattern of the synthesized nano-catalyst composed of $CuO/ZnO/Al_2O_3$ prepared by laser ablation route in water. Heterogeneity of the sample was examined to show their basicity and to confirm thehigh catalyticactivity that results in both high yield and short interaction time.

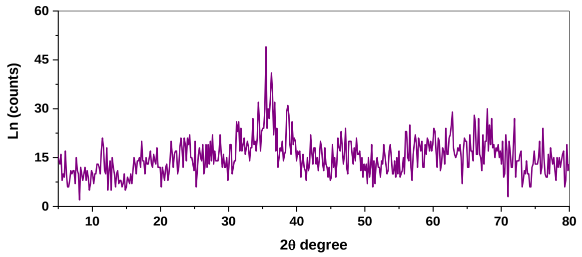


Figure (1) X-ray diffraction pattern of the synthesized nano-catalyst

To ensure the basicity of the sample and to estimate the concentration of the elements involved in the synthesis process of the catalyst can be determined using a portable XRF machine and listed in table (1)

Table 1. X-ray fluorescence (XRF) measurements

Element	%	+ / -
Cu	45.32	0.615
Zn	28.09	0.397
Al	10.20	0.157
Si	12.93	0.919
Other traces	3.48	0.102

3.2 Synthesis of 2-cyano-2-(p - nitrobenzylidene)-p -methoxyacetanilide) catalyzed by nanoCuO/ZnO/Al_2O_3

The Knoevenagel reaction of p-benzaldehyde and 2-cyano-N-(4methoxyphenyl) acetamide compounds catalyzed by $CuO/ZnO/Al_2O_3$ yielded the acetanilide portion. The impact of trial factors, including the types of impetus, were investigated to locate the best condition for this response and its outcomes. The $CuO/ZnO/Al_2O_3$ nanoparticles are the most effective impetus for the sonochemical amalgamation of an item and yield more than mass or squashed one **Figure.2.**

3.3 Optical Properties

UV-visible absorption spectroscopy is a valuable route that is used to inspect the optical description of nanoparticles, likewise used to additionally affirm the development of $CuO/ZnO/Al_2O_3$ nanoparticles. **Figure 3.**indicates the optical spectra of the organic product produced using both bulk and nano-catalysts. the spectra show obvious ingestion pinnacles of impetus nanoparticles at 338 nm from the Surface Plasmon Resonance (SPR). The arrangements framed after the laser removal have a green color characteristic of $CuO/ZnO/Al_2O_3$ nanoparticles. The force of the shading shifts relies upon the medium solution during the removal cycle. Removals in the assimilation top position reflect molecule size changes, and their recurrence relies upon the measure of nanoparticles framed.

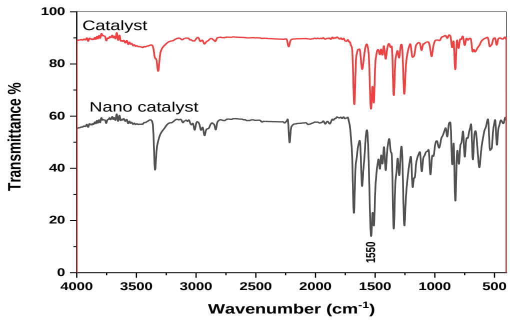


Figure (2) FT-IR transmittance spectral data of synthesized samples using bulk and nano-catalyst

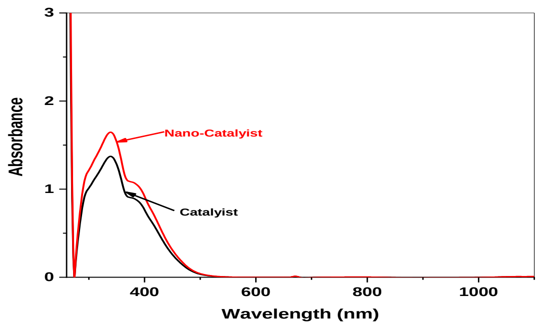


Figure (3) UV/Vis. spectral data of synthesized samples using bulk and nano-catalyst

3.4 Antibacterial Studies

The bactericidal activity of product synthesized by inorganic catalyst ($CuO/ZnO/Al_2O_3$) and organic catalyst (piperidine) were performed against gram-positive (*Streptococcus* bacteria) and gram-negative bacteria (*Enterococcus* bacteria) using the Agar diffusion method. The studied samples were seeded and incubated for 48 hours at 30 °CFigures4.a, and b. The antibacterial activity was assessed by measuring the inhibition zone and calculating the activity index as shown in Table 2.

Table 2. The activity index of product synthesized by inorganic catalyst ($CuO/ZnO/Al_2O_3$) and organic catalyst (piperidine)

Sample	**Activity index %**	
	Streptococcus **bacteria (gram-positive)**	***Enterococcus*** **bacteria (gram-negative)**
Catalyst (1)	90 %	90 %
Pipridine (2)	50 %	50 %

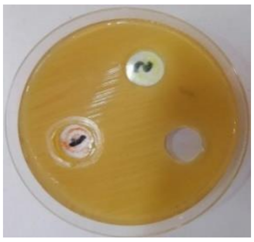


Figure 4.a Streptococcus**bacteria (Gram-positive)**

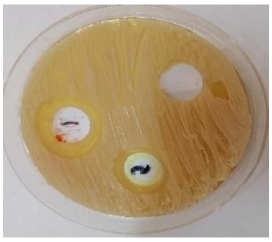


Figure 4.b Enterococcus bacteria (Gram-negative)

According to the equation, the proportion of antimicrobial activity has been computed. **[19]**:

% Activity Index =

$$\frac{zone of inhibition by test product (diameter)}{zone of inhibtion by standard\ (diameter)} X100$$

The bactericidal activities of the catalyst-prepared products indicate the highest values of activity index of inhibition for all two gram-positive and negative bacteria as compared to the control, which had a concentration of 30 μgmL^{-1}.

Figure 5 depicts the inhibition rate results from an in vitro activity index test.(2-cyano-2- (p -nitrobenzylidene) - p -methoxyacetanilide) inhibited gram-positive (*Streptococcus* bacteria) and gram-negative (*Enterococcus* bacteria). It was noticed also that the product synthesized using the inorganic catalyst ($CuO/ZnO/Al_2O_3$) against studied bacteria has an improved inhibition effect to about 90% relative to the standard antibiotic used while the inhibition rate of that synthesized using piperidine was only 50%.

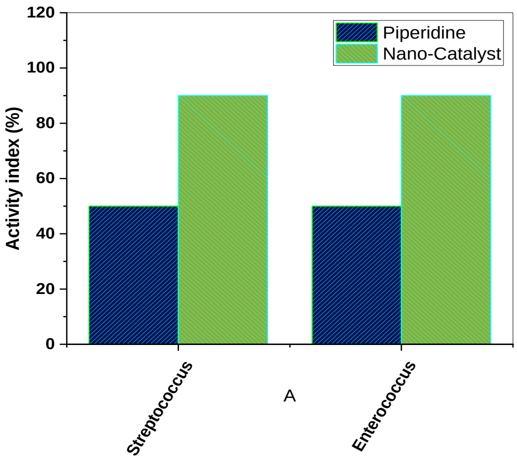


Figure 5 inhibition rate results from an in vitro activity index test

3.5 Reusability of $CuO/ZnO/Al_2O_3$ catalyst

$CuO/ZnO/Al_2O_3$ nanoparticles can be reused without losing their activity or weight. After the reaction has completed, filter the product and easily pack the catalyst particles, ethanol was added to wash the catalyst and remove the product. The repurposed catalyst was used in a new Knoevenagel reaction under similar reaction conditions, with the same weight as before. **Figure 6.**

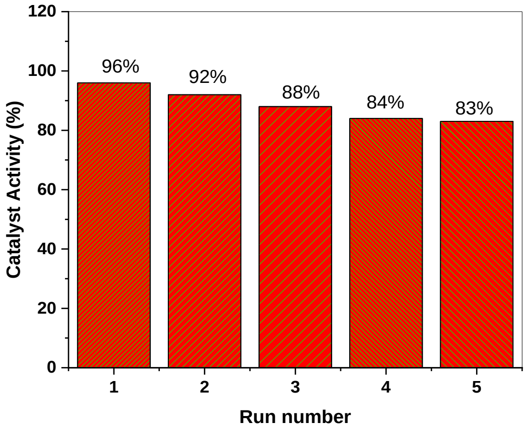


Figure (6) reusability test and catalyst activity versus the run number

4. Conclusion

The laser ablation route was successfully employed to synthesizea $CuO/ZnO/Al_2O_3$ glass-ceramic nano-catalyst in water. Synthesized nano-catalyst was used as a novel catalyst in the synthesis process of 2-cyano-2-(p - nitrobenzylidene)- p -methoxyacetanilide) by Knoevenagel condensation reaction. Highly efficient and recoverable nano-catalyst gives doubled yield. This new sonochemical offers many focal points like green processing, simple catalyst recoverability and reusability, high yields of different acetanilide compounds, and a fast time of reaction. In vitro antibacterial activity shows that the compound synthesized with the $CuO/ZnO/Al_2O_3$ catalyst has a higher potential antibacterial activity against the bacteria in comparison to the other.

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