Original Research Article

Synthesis and characterization of ZnO nano-particles and their application in synthesis of substituted quinoline

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Abstract

Nanotechnology is an emerging technology which can lead to a new revolution in every field of science. The interesting and sometimes unexpected properties of nanoparticles are largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material. Metal oxides are efficient heterogenous catalysts used in various organic transformations. The ability of nanotechnology to enhance catalytic activity opens the potential to replace expensive catalysts with lower amount of inexpensive nanocatalysts. The nano-ZnO as heterogenous catalyst has received considerable attention because of its inexpensive, non-toxic catalytic activity as as for eco-friendly behavior. In the present paper, the nanoparticles of ZnO are prepard by chemical method and the prepared nanoparticles are further used as catalyst for the preparation of ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate. The synthesized product was also characterized by spectral techniques.

Key Words: Nanotachnology, Heterogenous catalysts, Quinoline.

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INTRODUCTION

Metal oxides as heterogenous catalysts have been used in various organic transformations. The ability of nanotechnology to enhance catalytic activity opens the potential to replace expensive catalysts with lower amounts of inexpensive nanocatalysts. Zinc oxide is a low priced metal oxide which has been used in both industry and nano-type as a professional catalyst in various organic transformations.[1] Among the various methods available for synthesis of ZnO nanoparticles, the chemical precipitation and sol-gel technique were most effective because they provides suitable control of nucleation, ageing and growth of particles in solution. various researchers have attempted for the synthesis and characterization of ZnO nanoparticles. ZnO nanoparticles have found extensive uses in various industries including pharmaceutical, chemical, rubber, pigment etc. Recent survey[2-14] reveals that nano-ZnO as heterogenous catalyst has received considerable attention because of its inexpensive, non-toxic catalytic nature as well as the environmental advantages, minimum execution time, low corrosion, waste minimization, recycling and easy transportation.

MATERIALS AND METHODS

Synthesis of ZnO nanoparticles: In the present work the nanoparticles of zinc oxide were synthesized and further used as catalyst for the preparation of quinoline. ZnO nanoparticles were prepared by chemical co-precipitation method. 0.5 M zinc nitrate solution and 1 M urea solution are mixed slowly with contant stirring at 70^0C. The white cloudy solution obtained was centrifuged at 8000 RPM for 10 min. The product obtained was filtered, washed and calcined at 500^0C to separate the ZnO nanoparticles. The synthesized nanoparticles were characterized by X-ray diffraction analysis, scanning electron microscopy and the spectroscopic analysis of quinoline was also carried out. Prepared ZnO nanoparticles were then used as catalyst for the synthesis of quinoline derivative.

Synthesis of ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate: An equimolar mixture of 2-amino-5-chlorobenzophenone (1), ethylacetoacetate (2) and ZnO in ethanol medium was mixed with constant stirring. After completion of reaction the solid product was filtered, washed and recrystallized from ethanol to get the pure compound.

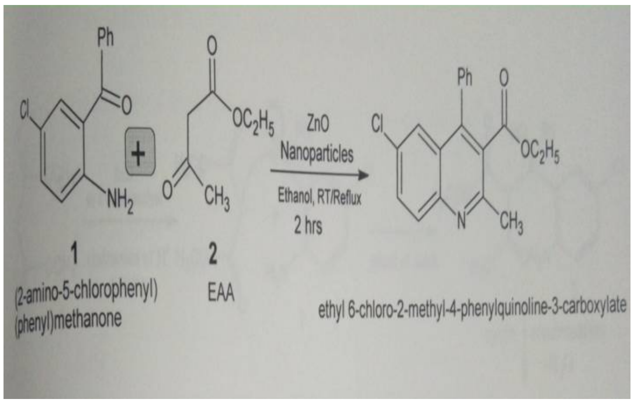

Figure 1:

RESULTS AND DISCUSSION

The characterization of ZnO nanoparticles was carried out using various techniques such as XRD and SEM.

Powder X-ray diffraction (XRD) studies: The powder XRD patterns of the ZnO nanoparticles is as shown in Fig. It is observed that the powder XRD patterns were indexed to pure hexagonal structure with the lattice parameter of a=3.25Å and c=5.2 Å nad its space group p63mc. The peaks obtained at different 2θ ranges correspond to pure ZnO and indicating tht the ZnO particles have crystalline structure. The average crystallite size was calculated using Debye-Scherrer equation.

$$D = K.\lambda / \beta \cos \theta$$

Where D is the diameter of the crystallite size, K is the shape factor (the typical value is 0.9), **λ** is the wavelength of the incident beam, **β** is the broadening of the diffraction line, measured in radians at half of its maximum intensity (FWHM) and **θ** is the Bragg's angle.

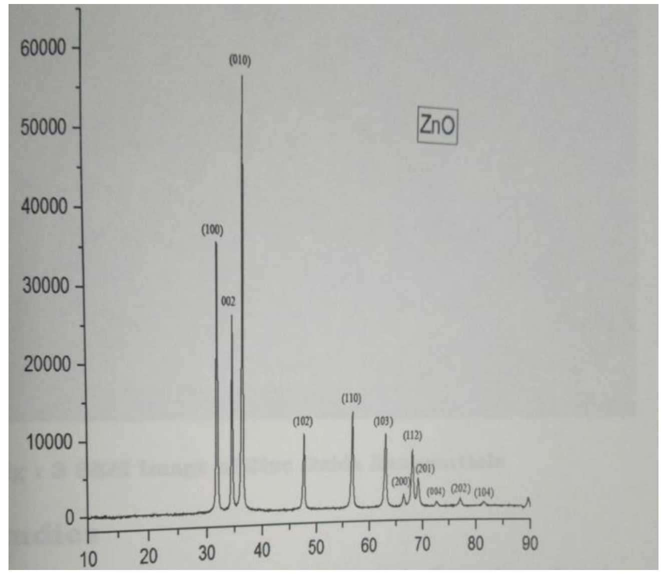

Figure 1:

X-Ray Diffraction Patternsof Zinc Oxide Nanoparticles: From XRD data, the average crystallite size was found to be 35 nm. No other peaks were observed in calcined compound, which indicates the formation of pure hexagonal structure of ZnO.

Scanning Electron Microscopy (SEM): Electron photomicrographs of the ZnO nanoparticles revealed that the synthesized particles were well defined and small spherical shaped with agglomerated particles. After the heat treatment at 500^0C for 3 hours, the ZnO particles were found in the range of 30-50 nm. It is observed that the particles mainly present as granules with small spherical shape and are well crystallized.

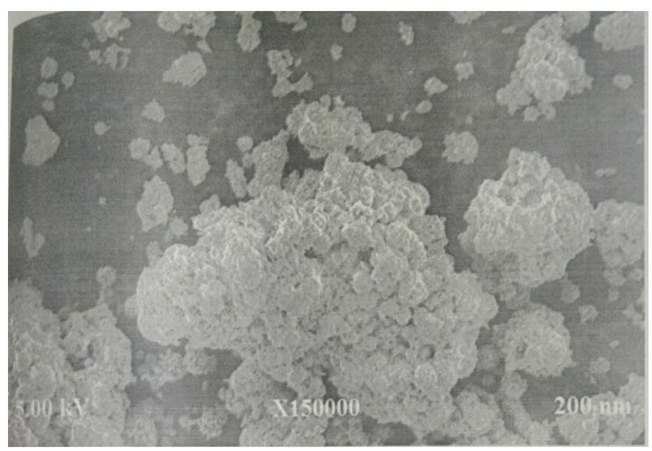

Figure 2:

SEM image of ZnO Nanoparticles Synthesis of ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate): The synthetic pathway follows Friedlander reaction mechanism. ZnO a base catalyst, abstract H^+ from ethylacetoacetate (1) to give an anion that attack on carbonyl carbon of benzophenone (2) to give adduct (3). This on cyclocondensation gave intermediate (4) which on dehydration followed by aromatization gives the desired quinoline derivative (5) as the final Friedlander reaction product. The obtained product was characterized by spectroscopic techniques.

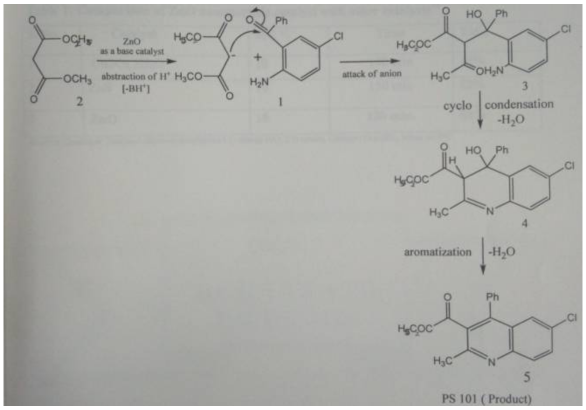

Figure 3:

Mechanism for the Synthesis of ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate

IR spectroscopic studies: The absorption spectra of ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate shows the C-N-H stretching and C-N stretching peaks at 3202 cm^{-1} and 1341 cm^{-1} respectively. Aromatic and aliphatic C-H strtching appears at 3085 cm^{-1} and 2840 cm^{-1} respectively. Peaks at 1749 is due to C=O stretching and peaks at 1557 cm^{-1}, 1439 cm^{-1} and 1036 cm^{-1} are due to C=C stretching and C=C bending respectively.

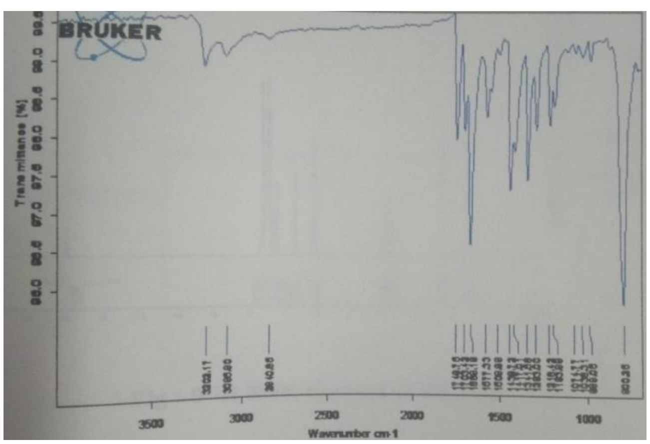

Figure 4:

IR Spectra of Product 1H NMR Spectroscopic studies: The ^{1}H NMR spectra of the product ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate shows the singlet (3H) at δ 2.31 ppm due to CH_3 protons attached to aromatic ring and peaks between δ 6.13-7.65 ppm due aromatic ring protons as multiplet (8H). Triplet (2H) at δ 1.99 ppm is due to CH_2 protons and quadrate (3H) at δ 3.99 ppm is due to CH_3 protons. Peak at δ 7.22 is due to residual solvent.

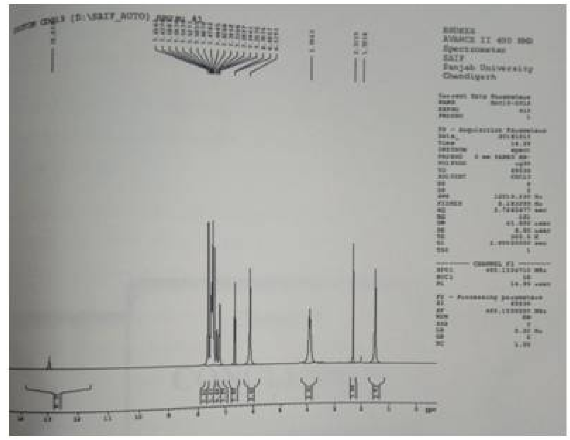

Figure 5: 1H NMR Spectra of Product

CONCLUSION

The ZnO nanoparticles were synthesized by chemical co-precipitation method and characterized by XRD, SEM and spectral techniques. The average size of nanoparticles is found to be 35 nanometer. The method used for the synthesis is environmentally friendly and economic. The prepared nanoparticles were used as catalyst for the synthesis of substituted quinoline in Friedlander reaction where ZnO has been found to show the better catalytic activity. It is evident from the present study that the synthesized nanoparticles may be used as green catalyst where other chemical catalysts have several drawbacks like handling, hazardous nature and tedious workup. Therefore, the ZnO nanoparticles acan be used as green catalyst for future reactions for heterocyclic synthesis.

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