Synthesis, characterization and catalytic activity studies of nano ZnO deposited on sintered calcium phosphate (ZnO/SCaP)

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Abstract-Nano ZnO was prepared by chemical methods on a novel solid support, namely, calcium phosphate .Different loading levels of nano zinc oxide over the support were prepared and influence of temperature on the synthesis was studied. The catalysts were characterized by physico-chemical methods. The XRD and UV-DRS showed formation of ZnO and high resolution SEM image showed formation uniform nano particles. The catalyst was found to be efficient in Knoevenagel condensation when compared with unsupported analogue.

Key words: Nano ZnO; SCaP support; Knoevenagel condensation, Coumarins, Bulk zinc oxide; Chemical deposition of ZnO; UV-DRS of ZnO.

1 INTRODUCTION

Zinc oxide has been reported to be an efficient catalyst in many organic reactions [1]. The structural changes at the nano level greatly influence the reaction rates [2, 3]. A large number of reports are available on the utility of nano zinc oxide [4, 5] in catalyzing organic reactions. In the design of a catalyst, the catalyst-support plays an important role for fixing the active-centre firmly, providing large surface area and imparting acidity to the catalyst. Conventionally, silica, alumina, zeolites, clay, etc., are used as catalyst-support. In the present investigation sintered calcium phosphate (SCaP) [6] was used as catalyst-support. The SCaP has P-O-P chains containing terminal P-O-H groups and cross-linked by calcium ions [7] and hence, it is expected to be acidic in nature.

2 EXPERIMENTAL

2.1 Preparation of catalyst-support (SCaP)

It involves forming a paste of calcium carbonate (precipitated 99%) using distilled water. To this paste, phosphoric acid was added drop-wise under continuous stirring. The reaction slurry was transferred to alumina crucible and dried in hot air oven at 150°C for 8 h. The dried content was sintered at 750°C for 30 minutes in a static air atmosphere using muffle furnace [6]. The sintered mass was then crushed to powder using mortar pestle and sieved through 325 mesh .The sieved powder was used as a catalyst-support for depositing ZnO..

2.2 Characterization

Powder X-ray diffraction was recorded by using GE Analytical XRD (Model: XRD 3003 T/T) 2θ value ranging from 10-70 degree. The SEM analysis was carried out using a Quanta Field Emission SEM (Quanta-200F). UV-visible spectra were recorded using Perkin Elmer spectrometer (LAMBDA-850 UV-Visible Spectrophotometer) in reflectance mode F.

2.3 Reaction

To a 50 ml round bottomed flask, calculated quantities of salicylaldehyde, ethylacetoacetate & ZnO/SCaP were introduced. It was fitted with double-walled condenser and cold water was circulated. The entire reaction set up was placed in oil bath and heated to desired temperature under continuous stirring using magnetic stirrer. The progress of reaction was monitored by TLC and the product distribution was analysed using HPLC.

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3 RESULTS & DISCUSSION

In the preparation of the catalyst, the zinc salt is precipitated as zinc hydroxide using the ammonia solution. If excess ammonia was added, the precipitate dissolves forming zinc complex. The volume of water used, the stirring speed and rate of addition of ammonia plays vital role in deciding the particle size of ZnO. The zinc hydroxide gets converted to zinc oxide at 125°C. Hence, 2 different temperatures were used for calcining the catalyst, viz., 150°C and 400°C. The XRD pattern of ZnO/SCaP (400) completely matches well with ZnO phase [8] (Figure 1) (PDF No. 891397) while, ZnO/SCaP (150) did not show formation of ZnO. This may be due to strong binding between zinc species on the support, which would have increased the decomposition temperature of zinc hydroxide.

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The SEM images also supported the XRD observation. The ZnO/SCaP calcined at 400°C showed formation of nano particles of ZnO with uniform particle size distribution in the range of 20 to 30 nm (Figure 3) while, that calcined at 150°C showed agglomerates without distinct particles (Figure 4). Hence, the calcining temperature of the catalyst was optimized as 400°C.

The UV-DRS spectra of ZnO/SCaP (400) showed a sharp absorption at around 380 nm. Dhakshinamoorthy *et.al*, [9] have studied absorption behaviour of bulk ZnO and nano ZnO. The bulk ZnO absorbed at around 300 nm while that of nano ZnO absorption between 380-400 nm. This observation was completely matching with the present study, where ZnO/SCaP (150) absorbed at around 300 nm corresponding to bulk ZnO and that calcined at 400°C showed absorption at around 400 nm corresponding to nano ZnO.

As a preliminary investigation evaluation of catalytic activity was carried out by taking 1.22 g of salicylaldehyde (1 eq.), 1.62 g of ethylaceto acetate (1.25 eq.), and 0.324 g of catalyst. This reaction mixture was subjected to heating at 120°C [10], under continuous stirring. The progress of the reaction was monitored by TLC (2% ethyl acetate & hexane). The influence of time was studied using different catalyst and the results are presented in Table 1. The conversion increases with reaction time and reaches 100% within 2 hours, whereas over bulk ZnO as a catalyst requires 10 hours for complete conversion. Reaction with blank catalyst-support (SCaP) showed 0% conversion.

The catalyst calcined at 150°C showed very low activity whereas the unsupported ZnO requires 8 hours for complete conversion .Thus, the ZnO/SCaP (400) was found to be superior in this condensation, in comparison with bulk ZnO.

TABLE 1

Knoevanagel condensation over ZnO/SCaP catalysts.

S.Nos	Catalyst	Time, hours	Conv. % (HPLC)	Yield of Coumarin %
1.	ZnO/SCaP(400)	1	95.3	72.0
2.	ZnO/SCaP(400)	2	100	77.3
3.	ZnO/SCaP(400)	3	100	96.0
4.	ZnO (bulk)	10	98	90.0

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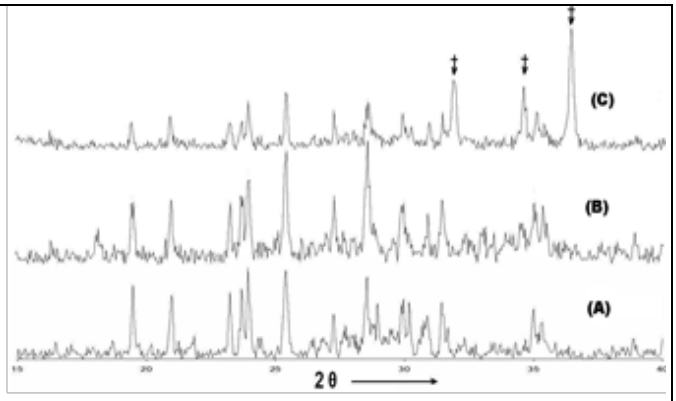

Figure 1: XRD patterns of (A) SCaP-750 (blank), (B) ZnO/SCaP(150) and (C) ZnO/SCaP(400)

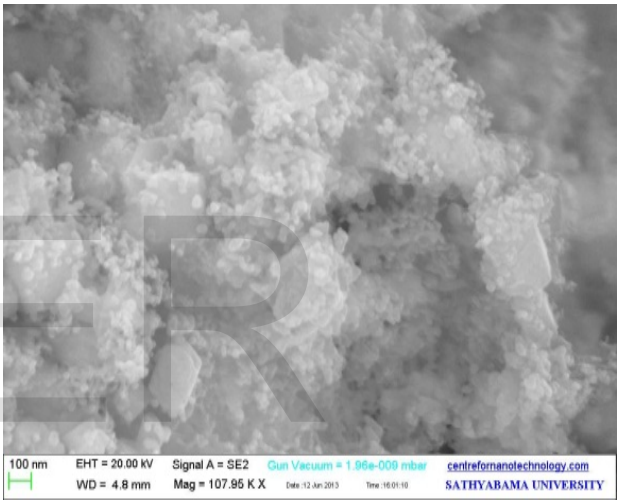

Figure 2: SEM image of ZnO/SCaP(400)

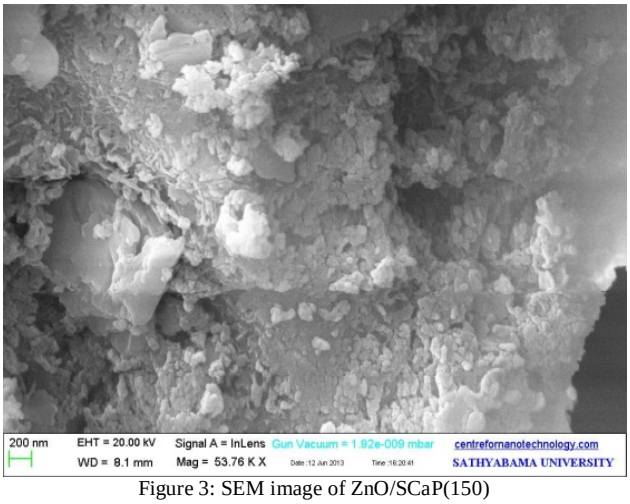

Figure 3: SEM image of ZnO/SCaP(150)

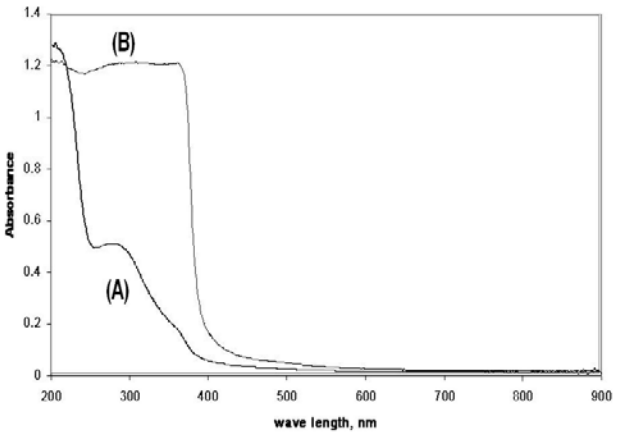

Figure 4: UV-DRS spectra of (A) ZnO/SCaP(150) and (B) ZnO/SCaP(400)

4 Conclusion

Nano ZnO was prepared over non-conventional support, namely sintered calcium phosphate. Influence of temperature during synthesis and physico-chemical characterization proved that ZnO/SCaP contains nano particles of zinc oxide. The catalyst was found to be efficient in Knovenagal condension with 100% conversion within 3 hours.

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