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An Innovative Approach for Efficient and Reusable Catalization for Synthesis of α, β-Unsaturated Compounds Using Polymer - NPs Composites as Catalyst

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Abstract. Catalyst plays an important role in many of synthesis and chemical reactions, like α,β-unsaturated products cannot be synthesized without presence of suitable catalyst, but for efficient catalization of reactions catalyst must have high surface area as well as they must be easily removed after termination of reaction without leaving an impurity in final product. To achieve both of these conditions an innovative approach is used. Here Polycarbonate (PC)-ZnO NPs composites membranes have been successfully fabricated by solution casting technique in where ZnO NPs (45nm) acts as a catalyst with increased surface area, while as these catalyst are embedded in PC matrix that can be easily removed after termination of reaction. Membranes were characterized via different techniques like SEM, FTIR etc. Activity of this nanocomposite based catalytic system for the stereoselective synthesis of α, β-unsaturated compounds is tested and found increased in yield of compounds with increase in concentration of ZnO nanoparticle content upto 5%. Above this at high ZnO loadings (9%) slight agglomeration of NPs occurred which hindered the catalytic effect of Nano composite.

Keywords: Ethyl lactate, α-β unsaturated compound, Polycarbonate (PC)-ZnO NPs composites, heterogeneous catalyst.
PACS: 78.67.Sc, 81.16.Hc, 81.16.Hc

INTRODUCTION

The α,β-unsaturated products have numerous applications in the synthesis of fine chemicals, natural products, functional polymers, calcium antagonists, perfumes and pharmaceuticals.Knoevenagel condensation, is a widely used reaction for the synthesis of α,β unsaturated carbonyl compounds[1] in the presence of an organic base which results in unwanted by-products due to polymerization and self condensations. The use of different types of heterogeneous catalysts such as aluminium oxide, MgO etc have been reported to avoid the use of organic bases and prevent the formation of byproducts. Nanoparticles due to high percentage of surface atoms can act as efficient catalyst for several reactions. .Nanoparticles must be immobilized on solid supports to prevent their aggregation and to facilitate the catalyst recovery [2]. Immobilized nanoparticles can be used for selective catalysis. Polycarbonate (PC) , due to transparency, dimensional stability, flame resistance, high heat distortion temperature, high impact strength, insoluble in a large majority of commonly used solvents and moisture insensitivity[3, 4] can be used as a solid matrix for ZnO nanoparticles.

We report herein the synthesis, characterization of ZnO/ polycarbonate (PC) nanocomposites and their catalytic application for efficient, leach free, stereoselective synthesis of α-β unsaturated compounds via Knoevenagel condensation in ethyl lactate (EL) under ultrasonic irradiation (Fig 1).

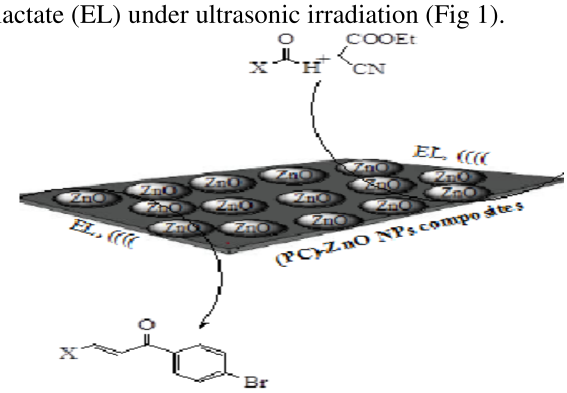

FIGURE 1: Synthesis of α,β-unsaturated compounds.

Solid State Physics
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EXPERIMENTAL

Catalyst Preparation

Polycarbonate granules are weighed and dissolved in dichloromethane (CH_2Cl_2) and stirred for 2-3 hours till a clear solution was formed. Then ZnO nanoparticles were dispersed in dichloromethane using ultra-sonicator. The resulting solution was then added to the polycarbonate solution and stirred for 30 minutes. The solution was then put into flat-bottomed Petri-dishes floating on mercury and solvent was slowly evaporated. The films so obtained were peeled off using forceps.

Catalyst Activity Measurement

A mixture of the aldehyde (1 m mol), ethylcynoacetate/ 4-bromo acetophenone (1 m mol), and ZnO/PC nanocomposite (5 mg) in 5 ml ethyl lactate was introduced in a 20 mL heavy walled pear-shaped two necked flask with non-standard tapered outer joint. The flask was attached to a 12 mm tip diameter probe and the reaction mixture was sonicated at ambient temperature for the specified period at 50% power of the processor and in a 4 s pulse. After completion of the reaction, the catalyst was filtered out. After removing the solvent in a rotary evaporator, the crude product was purified by recrystallization from ethanol.

RESULTS & DISCUSSION

XRD and SEM show the approximate spherical shape with the average diameter of about 45 nm for ZnO nanoparticles (Fig 2, 3). Polycarbonate (PC)-ZnO NPs composites were characterized by means of XRD, SEM and FTIR spectra. For both the membranes (with ZnO 5% and 9%), the XRD patterns indicated that the films revealed a polycrystalline hexagonal wurtzite crystal structure (a=3.2392, c=5.1986˚A) and a strong diffraction peak of ZnO (0 0 2), indicates that the membranes were successfully casted at low-temperature and highly oriented to the c -axis normal to the substrate (Fig 2). Fig 3 shows the morphology of catalytic system taken by SEM, These images shows in pristine membrane where no ZnO NPs are there have relatively smooth surface but as the ZnO NPs has mixed into the PC and their concentration is increased they comes at the surface of polymer. At 2% concentration few NPs are there on the surface but at 5% lot of NPs can be seen on the surface with homogeneous distribution of NPs if concentration of NPs are further increased NPs starts agglomeration as shown in the case of 9% doped catalytic system.

The peaks in the FTIR spectra show the chemical properties of PC-ZnO nanocomposite. A band at 500 cm-1 is attributed to the ZnO stretching band (Fig 4).

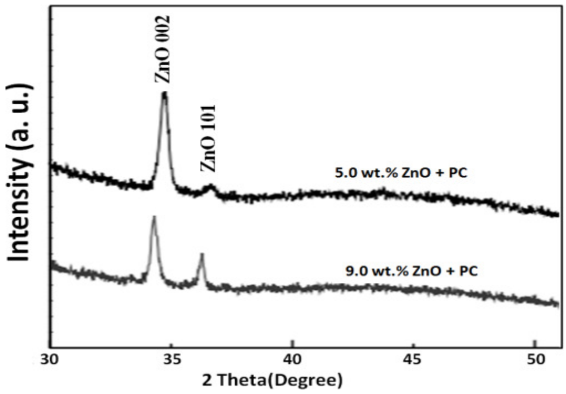

FIGURE 2. XRD spectra obtained from ZnO casted (5.0 wt.% and 9 wt.%) poly-carbonate membranes

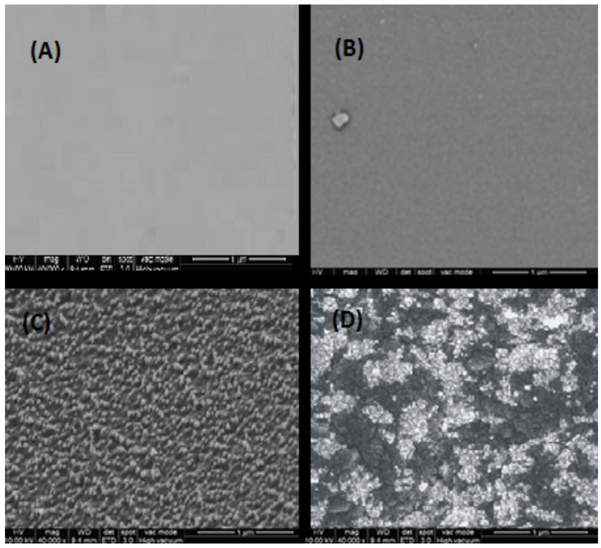

FIGURE 3. SEM images of Nano composite ZnO, polycarbonate membrans with various concentrations of ZnO (a) pristine membranes (b) 2% (c) 5% (d) 9%.

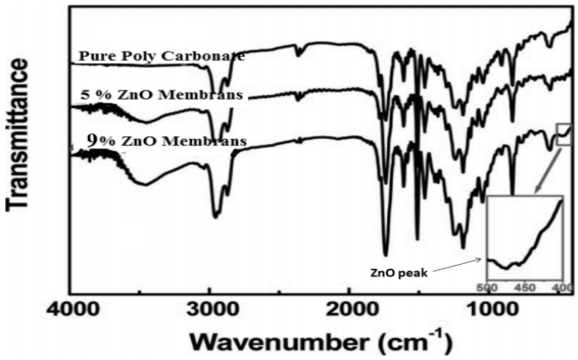

FIGURE 4. FTIR spectra of (PC)-ZnO NPs composites

Catalytic Activity for Knoevenagel Condensation

The Knoevenagel condensation of 4-chloro benzaldehyde with ethyl cyanoacetate was used as a model reaction in ethyl lactate under ultrasonic irradiation.Table1 shows the comparison of various catalysts. Using ZnO nanoparticles there was a sharp decrease in yield due to coagulation. To prevent agglomeration, ZnO NPs were immobilized on polycarbonate support. the study of catalytic ability of (PC)-ZnO NPs composites showed that loading of ZnO NPs in PC matrix increase the product yield to 98% and reducing the reaction time (4 min) with decrease the catalyst loading.

Interestingly, the yield increased smoothly with ZnO NPs loading up to 5%. When in PC matrix while ZnO NPs at higher loading (9%) ZnO NPs start agglomerates, which hindered the catalytic effect of Nano composite.

TABLE 1.

S. No	Condition	Time(min)	Yield (%)
1.	Blank	30	40
2.	ZnSO4 (10 mol%), US	20	60
3.	ZnCl2 (10 mol%), US	20	61
4.	ZnCl2 (10 mol%), US	20	68
5.	Powder ZnO(10 mol%), US	20	71
6.	ZnO NPs (10 mol%), US	14	78
7.	PC membrane	30	41
8.	(PC)-ZnO NPs composites (2%), US	4	86
9.	(PC)-ZnO NPs composites (5%), US	4	98
10.	(PC)-ZnO NPs composites (9%), US	4	85

CONCLUSIONS

(PC)-ZnO NPs composites were successfully synthesized by solution casting method. FTIR, XRD and SEM show the effective structural and chemical properties and confirm the doping of ZnO NPs in PC matrix. These nanocomposites created a new robust recyclable catalytic system for the stereoselective synthesis of α, β-unsaturated compounds. (PC)-ZnO NPs composites improved the reaction rate, product formation and catalyst recovery. It was found that the catalytic activity of the nanocomposites first increased with the increase in concentration of ZnO nanoparticles content up to 5% however, at high ZnO loadings (9%) slight agglomeration of nanoparticle occurred, which hindered the catalytic effect.

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