SYNTHESIS, CHARACTERISATION AND CATALYTIC STUDIES OF NANO ZINC OXIDE-ALUMINA FOR DISPLACEMENT REACTION ON CARBONYLDIIMIDAZOLE

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ABSTRACT

Nano zinc oxide supported on alumina was prepared by chemical method and calcined at 300 °C. The calcined material was characterized by UV-Visible spectroscopy, Infra-Red spectroscopy, X-Ray Diffraction technique, Scanning Electron Microscopy, Thermogravimetric analysis and Porosimetry. The catalytic activity studies on alumina supported zinc oxide for the synthesis of disubstituted ureas through displacement reaction on carbonyldiimidazole are hitherto unreported. Thus, alumina supported nano zinc oxide was tested for its catalytic activity in the displacement reaction of carbonyldiimidazole with cyclohexylamine. While, the above reaction when carried out at room temperature, afforded 1,3-Dicyclohexyl urea, as the sole product in 88% yield in 20 hours, at 80 °C, 1,3-dicyclohexyl urea was obtained in 80% yield, in 4 hours. Reusable and safer catalysts, reaction at room temperature, simple workup and product with good yield and purity are the merits of this process.

Keywords: Nano zinc oxide, alumina, SEM, XRD, carbonyldiimidazole, amines, disubstituted ureas.

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INTRODUCTION

Catalysts that promote reactions with remarkable regioselectivity, higher yield, shorter reaction time and significant turn-over number are ideal for their extensive utility in synthetic organic chemistry. Nano zinc oxide, one such catalyst fulfills the above requirements and the following few examples illustrate its applications in organic reactions. Catalytic conversion of isobutanol at 250 °C-400 °C over zinc oxide resulted in higher selectivity of dehydrogenation over dehydration.¹ Good stability of ZnO under highly acidic conditions, makes it more suitable in the three-component condensation, involving an aldehyde, β -keto ester and urea (Biginelli reaction).² In the Hantzsch condensation, it is reported that lesser reaction time and higher yield is more pronounced, with ZnO nanoparticles.³ Thus, nano zinc oxide, being a more effective catalyst, is employed in new C-C, C-P, C-N, C-S bond formations via Michael addition reaction⁴, in synthesis of organic carbonates⁵, in Friedel-Crafts acylation⁶⁻⁸ for the synthesis of aromatic ketones, in reaction of acid chlorides with alcohols / thiols / phenols⁹, Friedlander Quinolone synthesis¹⁰, etc. Nano ZnO has also been employed under solvent-free conditions in reactions in which, a higher yield (90 – 98 %) has been achieved.¹¹⁻¹² These partly accounts for the associated developments in the synthesis of nano ZnO.¹³⁻¹⁶ Still, not much has been reported on the use of ZnO NP in bulk or as ZnO NP on a suitable support, for the synthesis of substituted ureas. Symmetrical dicyclohexyl urea is a potent soluble *epoxide hydrolase* (sEH) inhibitor and known to lower systemic blood pressure.¹⁷ Also, cyclohexyl urea derivatives are known to exhibit antioxidant and antimicrobial activities.¹⁸ The available synthetic methods for substituted ureas mostly involve expensive catalysts such as Pd, Ru, Rh etc¹⁹⁻²⁰ and hazardous reagents such as azides²¹, isocyanates.²²⁻²³ Due to a limited number of cost-effective and eco-friendly methods²⁴⁻²⁸ and extensive application of urea derivatives²⁹, especially in pharmaceutical³⁰ and agricultural fields³¹⁻³⁷, continuous attention exists among the synthetic organic chemists towards developing effective methods for their synthesis.

The successful synthesis of unsymmetrical tetrasubstituted ureas, reported earlier from our laboratory involve the reaction of carbonyldiimidazole (CDI) with various types of amines, in presence of

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trimethylaluminium (AlMe_3).³⁸ This reaction, applicable to a large number of substrates, led to desired products in good yields and exhibited a good functional group tolerance. But a longer reaction time and a higher temperature associated with the pyrophoric nature of the catalyst made us search for a safe and alternative catalyst. ZnO being non-toxic, non-pyrophoric, safer to handle and versatile, it was thought that ZnO NP could serve as a substitute for AlMe_3 . Choosing alumina as the inert support, we synthesized ZnO on alumina by chemical method, characterized and studied its catalytic activity for the synthesis of dicyclohexyl urea through displacement reaction on CDI with cyclohexylamine. To the best of our knowledge, this is the first report on the synthesis of disubstituted urea using zinc oxide as a catalyst.

EXPERIMENTAL

All the chemicals, solvents and reagents used in this study were of laboratory grade/synthesis grade and used without any purification unless otherwise required. Characterization of ZnO on alumina was done by Thermogravimetry Analysis (TGA), Porosimeter, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Infrared (IR) and Ultraviolet-Visible (UV) spectrophotometry techniques. Thermogravimetry was done on a Q500 Hi-Res TGA unit equipped with a vertical furnace where a temperature ranges of $50\text{ }^\circ\text{C}$ – $900\text{ }^\circ\text{C}$ and a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ was employed. Here, sample purge gas used was high pure nitrogen. Micromeritics ASAP 2020 porosimeter was used to determine the BET surface area. Bruker D8 Advance Powder X-Ray Diffractometer was used for the XRD studies. The phase evolution of calcined powder was studied by using $\text{Cu K}\alpha$ radiation target at 40 kV and 30 mA and a with a scan rate of $10^\circ/\text{min}$. The data on 2θ was recorded in the range 10 – 90° . Jeol JSM-6390 Scanning Electron Microscope was used to characterize the mean particle size and morphology of the nanoparticles. The accelerating voltage of the microscope was kept in 20 kV. The optical absorption spectrum of zinc oxide nanoparticles was recorded using JASCO (V-350) Double Beam UV Visible Spectrophotometer at a scan speed of $400\text{ nm}/\text{min}$. The spectral bandwidth of Spectrophotometer was 5 nm and the scanning in the wavelength range of 200 to 900 nm was done with a data interval of 1 nm.

Progress of the reactions was monitored by using Thin Layer Chromatography using Aluminum backed, silica gel TLC plate coated with fluorescent indicator F_{254} . Ethyl acetate and n-hexane mixture (3:2) was used as the eluent. Melting points reported for the crude products are uncorrected. The ^1H NMR and ^{13}C NMR spectra were recorded on a Jeol FX200 spectrometer using TMS as internal standard and $\text{DMSO-}d_6$ as a solvent. FT IR of the sample as KBr pellet was recorded on JASCO FT/IR-410 infra-red spectrometer.

RESULTS AND DISCUSSION

Synthesis of Zinc oxide-Alumina

The catalyst, zinc oxide-alumina was prepared by precipitation method as described below. In a 2 L beaker, 7.52 g of neutral alumina and 6.63 g of zinc acetate dihydrate were placed and 800 mL of water was added. This mixture was stirred well using a mechanical stirrer. 2.65 g of sodium hydroxide was dissolved in 100 mL of water. To the mixture containing zinc acetate and alumina, under stirring, the sodium hydroxide solution was added slowly over 80 minutes. The reaction mass appeared as a milky white suspension. After the complete addition of the sodium hydroxide solution, the contents were heated over a water bath kept at $90\text{ }^\circ\text{C}$, for two hours. A white precipitate formed was allowed to settle (30 minutes). Decantation of the supernatant liquid and subsequent filtration under vacuum, afforded zinc oxide-alumina as a white solid mass. This was washed with ethanol ($2 \times 25\text{ mL}$) followed by water ($2 \times 25\text{ mL}$) and then dried at room temperature for two hours. Further drying was done in a hot-air oven maintained at $120\text{ }^\circ\text{C}$ for two hours. Then, calcination was done at $300\text{ }^\circ\text{C}$ for three hours in a muffle furnace. This calcined zinc oxide-alumina obtained as a white powder (8.58 g, 86 % yield) was characterized and their details are given below.

Characterization of Zinc oxide-Alumina

The SEM images of $\text{ZnO-Al}_2\text{O}_3$ sample (Fig.-1) showed rod-shaped particles with an average particle size of approximately 50 nm. The support material, alumina is not visualized in the SEM picture and this may probably be due to the amorphous nature of the support.

Fig.-1: SEM: ZnO NP supported on Al_2O_3

The crystallinity of the synthesized ZnO NP is reflected by the peaks with well-defined shape in X-Ray Diffraction Spectrum (XRD) (Fig.-2). The peaks corresponding to 2θ values of the sample, resemble ZnO wurtzite structure (JCPDS Data Card No: 36-1451) and the purity of the sample is good, as evidenced by the absence of peaks other than that of ZnO.³⁹ Here again, diffraction peaks, characteristic of alumina were not seen. It is important to mention here that alumina doped zinc oxide synthesized elsewhere by coprecipitation technique or by hydrothermal route, exhibited relatively broad peaks corresponding to zinc oxide with low intensity⁴⁰⁻⁴¹. The nanoparticles crystallite sizes calculated from X-ray line broadening using Debye–Scherrer equation for the strongest three peaks at 2θ 32.0, 34.67 and 36.5 were about 26.28 nm, 26.63 nm and 30.06 nm respectively.

Fig.-2: XRD Spectrum of ZnO- Al_2O_3

UV-DRS spectrum of ZnO- Al_2O_3 NP in Fig.-3 reveals the absorbance peak in the range of 350 -380 nm corresponding to the characteristic band of ZnO NP⁴². This is also in accordance with the reports available in the literature on the UV spectral characteristics of ZnO NP.⁴³⁻⁴⁵

Fig.-3: UV-Vis Spectra of ZnO- Al_2O_3 NP

Whereas aluminium doped ZnO NP has been reported to exhibit a blue shift in the UV absorption attributed to the direct transition of electrons in the ZnO nanocrystals. The absence of such observation in UV absorption may probably due to the insignificant structural influence of Al_2O_3 on ZnO in the present

study. In FTIR spectrum of the ZnO-Al₂O₃ NP, the peak at 543 cm⁻¹ corresponds to the characteristic absorption of Zn-O bond and the broad absorption peak at 3398 cm⁻¹ and a peak at 2363 cm⁻¹ is attributed to hydroxyl and C=O groups, probably due to moisture and carbon dioxide respectively.⁴⁶⁻⁴⁷ In thermogravimetric analysis (TGA), when ZnO-Al₂O₃ NP was heated from room temperature to 900 °C under nitrogen atmosphere, a significant weight loss (6.34%) was observed in the range of 30 °C-300 °C (Fig.-4). Further weight loss in the wide range of 300 °C-900 °C was about 4.06%. In the TGA of the sample, a peak was observed between 90 °C-150 °C and this may be due to loss of absorbed water and another peak observed around 330°C may be attributed to the oxidation of organic materials. In effect, there was an overall steady decrease in weight loss with an increase in the temperature.⁴⁸ Porosimetry studies done for the ZnO-Al₂O₃ NP revealed a BET surface area of 74.1369 m²/g. The average pore volume of pores less than 190 nm (P/P₀ = 0.9897) was 0.1676 cm³/g and the pore size was found to be 52.601 Å.

Fig.-4 Thermogravimetric Analysis of ZnO-Al₂O₃ NP

Catalytic Activity of ZnO-Al₂O₃ NP in Displacement Reaction on CDI

The synthetic utility and catalytic activity of the prepared ZnO-Al₂O₃ NP were assessed by displacement reaction on CDI (water-soluble) with cyclohexylamine as follows. A solution of CDI (1 equiv.) and cyclohexylamine (1 equiv.) in 20 mL toluene, kept at room temperature for 144 hours, afforded the expected product symmetrical dicyclohexyl urea (DCU) in negligible quantity. Reactants mixed with 0.05 equivalents of neutral Al₂O₃ and stirred at room temperature for 14 hours did not lead to any reaction. The poor reaction in the absence of ZnO signifies that there is an interaction of the catalyst species ZnO, with the substrate, CDI, thereby enhancing the nucleophilic attack at the carbonyl center. The reaction in neat, carried out in presence of 0.08 equivalents of the catalyst (ZnO-Al₂O₃), at room temperature for 14 hours, under unstirred conditions, afforded the product, DCU in 1.78% yield. As the support material is in the amorphous state, diffusion of the reactants through the solid surface containing the active species, ZnO is difficult and this might delay the formation of CDI-catalyst complex and hence, a poor yield.

The successful synthesis of DCU catalyzed by ZnO-Al₂O₃ is described below. To CDI (1 equiv.) taken in 20 mL toluene, CHA (2 equiv.) and ZnO-Al₂O₃ (0.08 equiv.) were added and then stirred at room temperature for 14 hours. Thin Layer Chromatographic analysis (3:2 EtOAc-n-hexane) of the reaction mixture after 14 hours, indicated the presence of CDI (R_f = 0.175), a new spot at R_f = 0.075, but the spot corresponding to cyclohexylamine (R_f = 0.375) was not seen (Scheme-1).

Toluene was removed from the reaction mixture by filtration and the solid mass was washed with water and filtered. The solid product mass containing the catalyst was extracted with methylene dichloride (10 mL) and filtered to separate the catalyst. The catalyst was washed with 2 mL methylene dichloride followed by 10 mL of water, then dried in a hot air oven at 110 °C for 2 hours and labelled as recovered catalyst. The organic layer was dried over anhydrous sodium sulphate. Removal of the solvent afforded a white solid mass. It was dried at room temperature for 1 hour and then dried at 100 °C for 3 hours (74.4% yield, Scheme-1). This product melted at 230 °C (Lit. M.P. of 1,3-Dicyclohexyl urea = 229 °C - 230 °C⁴⁷).

TLC of this isolated crude product showed a single spot with $R_f = 0.075$. The ^1H NMR spectrum of the product indicated the characteristic proton signals ($-\text{NCH}$ at 3.4 ppm; $-\text{NH}$ 5.4 ppm). The ^{13}C NMR spectrum showed urea carbonyl ($-\text{N}-\text{C}(=\text{O})-\text{N}-$) at 157 ppm and $-\text{NCH}$ at 34 ppm. The IR spectrum indicated the presence of peaks due to $-\text{NH}$ in the region of $3250\text{ cm}^{-1} - 3600\text{ cm}^{-1}$ as well as due to urea carbonyl.

Scheme-1: $\text{ZnO-Al}_2\text{O}_3$ Catalyzed Synthesis of Dicyclohexyl Urea

It is to be noted that in the above reaction, either the use of four equivalents of cyclohexyl amine or performing the reaction under closed conditions has no significant influence on the yield of DCU. A mixture of CDI (1 equiv.), cyclohexylamine (1 equiv.) and 0.03 equivalents of the ZnO (bulk) in 20 mL toluene, when stirred for 14 hours led to the product DCU in 67.4% yield. The optimum reaction time for maximum yield of the product in the $\text{ZnO/Al}_2\text{O}_3$ catalyzed reaction is 20 hours (Fig.-5). Increase in reaction time from 20 hours to 28 hours, though resulted in complete consumption of starting material (by TLC), it has not led to significant improvement in the yield. Decomposition of the reactants or loss of catalytic activity due to slow poisoning during the longer reaction time, either by cyclohexylamine or by the product may account for the observed loss in reaction yield. Also, no significant change in the yield was observed, even with a two-fold increase in the quantity of the catalyst (Fig.-6).

Fig.-5: Influence of Reaction Time

Fig.-6: Influence of Catalyst Quantity

This may be due to the blocking of the active sites caused by the strong adsorption of the product and the amorphous nature of the support that results in a reduced diffusion rate. In the studies on the effect of solvent on the reaction yield (Table-1), it is inferred that polar solvents led to a lower yield of the product. Among the solvents employed, the preferred solvent is toluene, where the reaction yield (74.4%) was the highest in 14 hours. Reduction in yield of the product by 10% - 15% was observed when the recovered catalyst was reused.

It is significant to mention here that in synthesis involving condensation of *S, S*-dimethyl dithiocarbonate reagent with cyclohexylamine, the reaction occurred at 65°C and DCU was obtained in 65% yield⁴⁹ and it yet another report, DCU was prepared in good yield from urea and cyclohexane but multiple devices are required and the reaction requires a temperature as high as 180°C ⁵⁰. In the present study, while the reaction of CDI (1 equiv.) with CHA (2 equiv.) in presence of $\text{ZnO-Al}_2\text{O}_3$ NP (0.08 equiv.) at room temperature for 14 hours afforded DCU in 74.4% yield, reaction at 50°C resulted in an increase in yield (81.25%) associated with a decrease in reaction time (8 hours). Under the conditions of reflux, though the

reaction got completed in 4 hours, the yield has not improved (80 %). A 20% loss in yield could be attributed to the decomposition of the starting materials or products under the reaction conditions.

Table-1: Influence of Solvent on Reaction Yield

S. No.	Solvent	Yield (%)
1	Water	24.10
2	Acetone	32.14
3	Dioxane	41.07
4	THF	42.85
5	Ethyl acetate	45.09
6	EDC / MDC	51.79
7	Acetonitrile	54.91
8	Cyclohexane	66.52
9	Toluene	74.40
10	Neat, solvent-free	38.84

Reaction conditions: CHA (2 equiv.) + CDI (1 equiv.) + ZnO-Al₂O₃ (0.08 equiv.), 14 hours, room temperature

CONCLUSION

Zinc oxide-alumina, synthesized by the chemical method was characterized by UV-Visible, IR, TGA, XRD, SEM and porosimetry. The support material appeared to be non-crystalline and ZnO NP synthesized corresponds to Wurtzite structure and the pore size of the NP was 50 nm. The catalyst is active and is highly useful for the synthesis of 1,3-dicyclohexyl urea. The reaction at room temperature involving a cheap and safe catalyst, simple workup and crude product with reasonable purity are the merits of this synthesis. The optimum and mild conditions that can be employed for maximum yield of the product, dicyclohexyl urea (88.8%), corresponds to the reaction of CDI (1 equiv.) with CHA (2 equiv.) under stirring in toluene as solvent, at room temperature for 20 hours.

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