

Solvent Free Synthesis Of N,N-Diethyl Hydroxyl Amine Using Glycerol-Stabilized Nano – TiO₂ As An Efficient Catalyst

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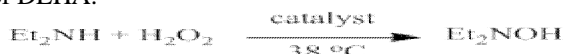
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ABSTRACT: The development of green and economical procedures for production of chemicals is an important research subject in chemistry. The use of nanocatalysts in various organic synthesis not only meets the goals of green chemistry, but also increase the yield of the reaction. N,N-diethyl hydroxyl amine has been interesting to us because of its action as corrosion inhibitor. In this study, catalytic activity of glycerol-stabilized nano-TiO₂ for the synthesis of N,N-diethyl hydroxyl amine under solvent free condition has been investigated. Glycerol-stabilized nano-TiO₂ has been successfully synthesized by sol-gel procedure and characterized by scanning electron microscopy (SEM). The direct nanocatalytic process was used for preparation of N,N-diethyl hydroxyl amine by means of the oxidation of diethyl amine with H₂O₂. The effect of reaction time, temperature and amount of nanocatalyst was studied and optimum conditions (Temp.:35°C, time:45min. and 75 mg) were selected. The gas chromatography with flame ionization detector (GC-FID) was used for quantification of N,N-diethyl hydroxyl amine during its synthesis investigations.

KEYWORDS: Corrosion, oxygenscaveng, N,N-diethyl hydroxyl amine, solvent less, glycerol-stabilized nano-TiO₂, DEHA

I. INTRODUCTION

Nano matter is expected to be a fruitful area of green chemistry catalysis due to the increasing ability to design in the nano scale and the high surface areas found in nano materials. Nanocatalysts are esteemed as materials of enormous surface areas and with new research, developments expanding catalytic capabilities may be offered. Nanocatalysts are heralded as new process, candidates exhibiting higher activity, greater stability, durability or recycling potential, efficient recovery characteristics, and cost effectiveness. These new catalysts are candidates for clean energy applications such as hydrogen generation, hydrogen storage and fuel cell applications[1]. One of the promising nano catalyst applications is the synthesis of DEHA.



N,N-diethylhydroxylamine (DEHA) as an important synthetic material is commonly used in water treatment chemical formulation for controlling corrosion(oxygen scavenger), photographic chemical, inhibitors and silicone rubbers[2]. In spite of its great conveniences, the preparation of DEHA is an important challenge for organic chemists. Several methods for synthesizing N,N-dialkyl-hydroxylamines are already known. Particularly, the nitrones can be reduced either to disubstitutedhydroxylamines by means of lithium aluminum hydride or by means of potassium boro-hydride or by hydrogenation on platinumblack[3]. The N,N-dialkyl-hydroxylamines may also be prepared either by the reaction of compounds containing a N-O bond, by allowing said compounds to react with organometallic compounds[4] or by alkylation of hydroxylamines or N-alkylhydroxylamines with alkyl halogenides[5]. The other method can be very much improved by carrying out the oxidation of the corresponding amine by means of hydrogen peroxide in the presence of a particular catalyst[6]. In this paper, we utilized the last method mentioned in the presence of glycerol-

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stabilized nano-TiO₂ and investigated optimum reaction temperature and amount of nano particle used. The important feature of this synthesis is the absence of solvent at the reaction.

II. PROPOSED METHODOLOGY

Reagent

Diethylamine (DEA, 85%, Daejung), Hydrogen peroxide(30%, fluka), Calcium chloride for dehydration, titanium isopropoxide, isopropanol, acetic acid, glycerol and distilled water have been used in this work.

Procedure

The apparatus was charged with 2 ml of Diethylamine, 75 mg of glycerol-stabilized nano-TiO₂. The suspension, kept under continuous reflux and stirring by means of a magnetic stirrer, was heated at 30-40 °C. After that, dilute hydrogen peroxide was added (at 30% by weight) by syringe. The addition was completed within 45 minutes. When the addition was over, the solution was cooled and dehydration by calcium chloride for GC analysed.

Preparation of glycerol-stabilized nano-TiO₂

The glycerol-stabilized nano-TiO₂ was also prepared by the sol-gel method as reported in the literature [7]. 5 ml titanium isopropoxide was dropped into the solvent mixture (isopropanol and acetic acid with optimum ratio 3:8) and stirred at room temperature. The mole ratio of alkoxide/water and alcohol/acetic acid are of high importance and need to be adjusted. So, the mole ratio of alkoxide/water was 1:1 and alcohol/acetic was 3:8. Then, 5 ml deionized water was added to the alcohol, acetic acid and alkoxy mixture for hydrolysis of alkoxide. A milky slurry mixture was appeared. 1 ml glycerol was added into the above mixture and mixed by ultrasonic for 3 h. The obtained mixture was heated at 60 °C for 5 h in order to evaporate excess water and solvent. After that, the as-prepared precipitation was dried at 100 °C for 10 h and then The samples were calcined at 500 °C for 5 h.

GC-FID analysis

GC/FID was carried out using a gas chromatograph, Agilent America US10611009 series with flame ionization detector (FID) and head space analyser using a DB-624 column (60 m, 0.25 mm, film thickness 1.4 µm) coated with dimethyl polysiloxane and Cyanopropyl-phenyl. The oven temperature was programmed from 60 to 220 °C at 15 °C/min, with the injector temperature at 200 °C and detector temperature at 250 °C. Injection volume was 0.5 µl. Nitrogen was used as a carrier gas (1.0 ml/min).

III. EXPERIMENTAL RESULTS AND DISCUSSION

Morphology

The morphology analysis of samples was achieved using a scanning electron microscopy (LEO 1430VP).

Fig 1 illustrates SEM image of glycerol-stabilized nano-TiO₂. It can be seen that nanoparticles has irregular spherical and cubical shapes.

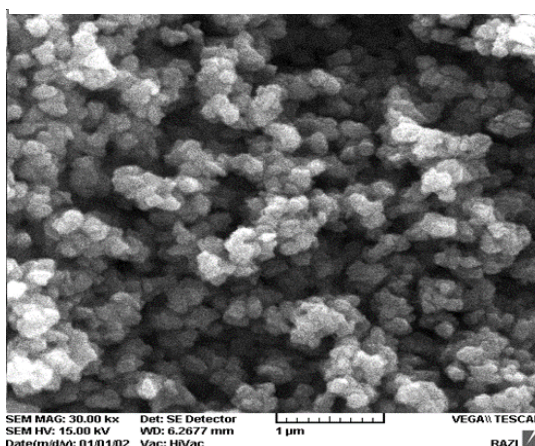
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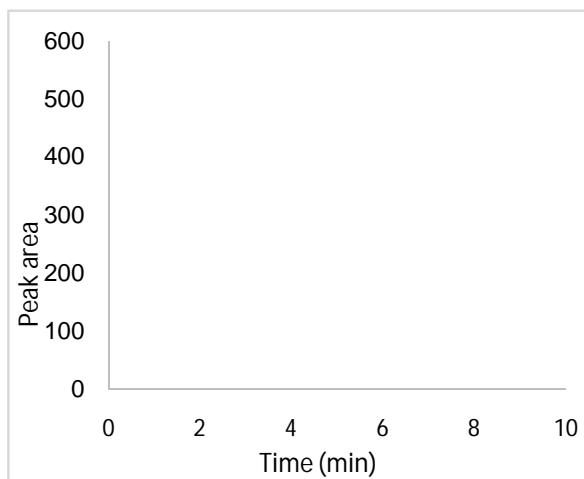
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Fig. 1. SEM image of glycerol-stabilized nano-TiO₂



The goal of this work was the synthesis of DEHA without solvent. Results of GC-FID verified DEHA is shown in Fig2.

Fig. 2. results of GC-FID analysis of DEHA synthesis



As shown in Fig 2, the blue graph is synthesized samples and the red graph is the reference sample. A peak value appeared on 6.4 minutes in both graphs, shows the concentration of DEHA.

Optimization of temperature

Temperature is one of the most important parameters in every system and process that can play a major role in advancing reactions. In order to investigate the effect of temperature on the synthesis of DEHA, several temperature conditions were applied to reach the highest efficiency. Fig 3 depicts the optimization diagram of temperature for synthesis of DEHA. It can be seen from Fig 3 that the highest percentage of DEHA can be obtained at 38 °C. There is

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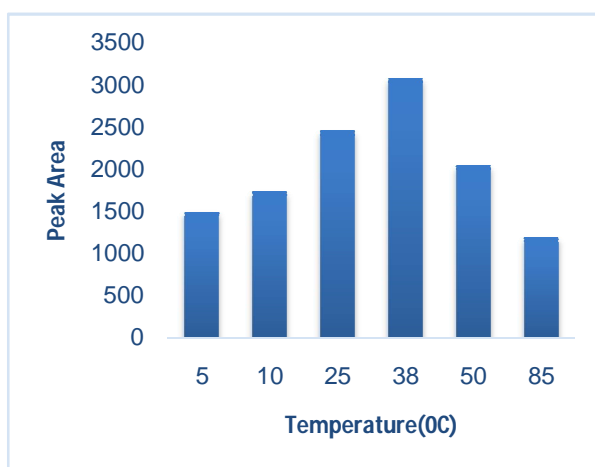
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the lowest yield at 85 °C that can be attributed to the decomposition of diethyl amine (the boiling point of diethyl amine is 56°C). All conditions except temperature were fixed.

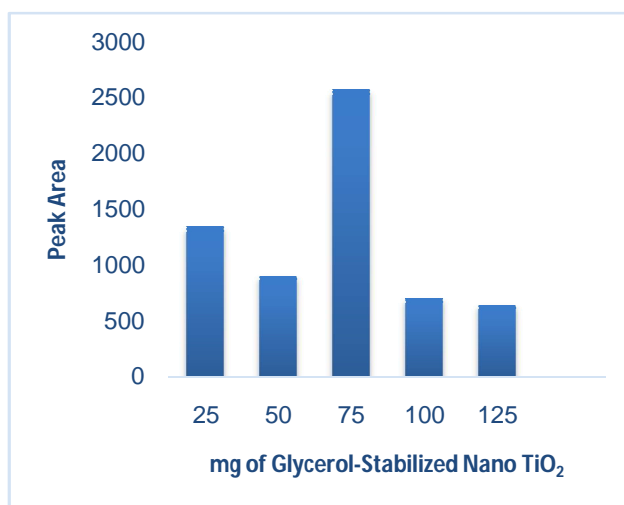
Fig. 3. Optimization of temperature with glycerol-stabilized nano-TiO₂ as catalyst



Optimization of the amount of glycerol-stabilized nano-TiO₂

In order to achieve high purity of DEHA synthesis, we optimized amount of nano particles used (Fig 4).

Fig. 4. optimization amount of glycerol-stabilized nano-TiO₂



In 75 mg of the nanoparticles, the maximum amount of DEHA was synthesized.

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IV. CONCLUSION

The aim of this study was synthesis of DEHA by a nano-catalyst. According to the results of the analysis of GC-FID, DEHA with maximum purity was obtained. Also, this valuable material could be synthesized by optimizing the temperature and amount of nano catalyst materials without any solvent. The solvent free synthesis has an advantage that the effective collisions between reagents increases, therefore the yield of reaction increases.

REFERENCES

- [1] J.A. Glaser, , Green chemistry with nanocatalysts, pp.513-520, 2012.
- [2] N,N-diethylhydroxylamine - Compound Summary, PubChem Compound. USA: National Center for Biotechnology Information, 27 March 2005. Identification. Retrieved 17 March 2012.
- [3] O. Exner, Derivatives of oximes. II. Reduction of O-and N-alkyl oximes with lithium aluminium hydride, Collection of Czechoslovak Chemical Communications, 20.1, pp. 202-209, 1955.
- [4] Hepworth, Harry, The action of the mmobili reagent on certain nitric esters, J. Chem. Soc., Trans, 119, pp. 251-260, 1921.
- [5] Bader, Henry, Preparation of alkylated hydroxylamines, U.S. Patent No. 3,491,151., 1970.
- [6] Roffia, Paolo, et al, Reacting corresponding secondary amine with hydrogen peroxide, titanium-silicate catalyst, U.S. Patent No. 4,918,194. 17., 1990
- [7] T. Tran, W. Jei Cho and C. Sik Ha, Preparation of TiO₂ nanoparticles in glycerol-containing solutions, Materials letters, 57.18, pp. 2746-2750, 2003