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Spectroscopic Validation and Catalytic Efficiency of Ionic Liquid-Mediated Terpyridines and Zirconia-Based Catalysts in Green Organic Synthesis

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Abstract

Background: *Heterocyclic compounds of nitrogen, including terpyridines, are commonly utilized in catalysis, materials science and pharmaceuticals, whereas traditional methods of synthesis require hazardous conditions.*
Methods: *The study employed a green synthetic approach was used, where ionic liquids and modified zirconia catalysts were used in the solvent-free, microwave-assisted reaction. The products of the synthesis were analyzed by ^{1}H NMR, ^{13}C NMR, GC-MS, CHNS, PXRD, FT-IR, and BET.*
Results: *Spectroscopic analysis revealed that it had been synthesized successfully in high purity. Catalytic experiments indicated that sulfated and borate zirconia catalysts enhanced yields of a reaction by more than 95 percent in 15-20 minutes. The highest performance was noted at 650 o C calcination temperature and the right amount of catalyst.*
Conclusion: *The designed approach offers an effective, environmentally friendly, and scalable approach to synthesize heterocyclic compounds that have improved catalytic activity.*

Keywords: *Green synthesis, Terpyridines, Ionic liquids, Zirconia catalysts, Microwave-assisted reactions, Heterocyclic compounds.*

INTRODUCTION

Heterocyclic compounds containing nitrogen take a central role in the contemporary chemistry because of the high number of applications in pharmaceuticals, catalysis, and even complex materials. The terpyridines and substituted pyridine derivatives are among these with much attention drawn to their structural flexibility and high affinity in coordinating with metal ions. Specifically, 4 (pyridyl) terpyridines have found applications as ligands in supramolecular chemistry and functional materials, and triarylpyridines and analogues have potential biological, optical and electronic applications [1,2]. The study of effective synthetic procedures of such compounds is thus a significant field of study. Traditional synthetic methods of terpyridines and pyridine derivatives tend to be multistep reactions, severe reaction conditions, and use of toxic organic solvents. Such restrictions not only decrease the overall efficiency but also increase environmental and safety issues. The increased focus on green chemistry in recent years has led to the exploration of alternative methodology, which is environmentally benign, cost-effective and operationally uncomplicated. Among them, ionic liquids and solid acid catalysts have become a strong solution to the problem of the replacement of volatile organic solvents and the enhancement of reaction rates. Their low vapor pressure, high thermal stability and capacity to dissolve broad reactant range make ionic liquids especially appealing. Likewise, zirconia catalysts have been modified and have been widely studied in terms of acidity and catalytic activity with excellent acidity and activity. The structural features of such catalysts, such as phase composition and surface features, are important factors that define their efficiency [3].

Such methods as PXRD and FT-IR analysis are also important indicators of catalyst structure, whereas BET analysis can be used to learn more about surface area and porosity which are direct determinants of catalytic behaviour. Moreover, it has more enhanced reaction efficiency through the use of the solvent-free conditions that use microwaves as the heat source that has in turn shortened the reaction time and has also enhanced the yield of products.

Green solvents plus solid acid catalysts and microwave irradiation provide an environmentally friendly solution to the preparation of complex heterocyclic compounds. In spite of these improvements, systematic assessment of the correlation between catalyst structure, reaction conditions and product yield is required to implement a consistent and scalable synthetic protocol [3,4]. To explore the synthesis, spectroscopic characterization, and catalytic performance of terpyridine analogs with modified zirconia catalysts under green and solvent-free and microwave-assisted conditions.

Methods

This research was carried out in an experimental way of lab synthesis and assessment of 4 7 -(pyridyl) terpyridines and other similar catalyst systems under green chemistry circumstances. Reagents, such as 2-acetylpyridine, pyridine carboxaldehyde, substituted acetophenones, and aromatic aldehydes, were prepared without additional purification. As a source of nitrogen, ammonium acetate was used, and sodium hydroxide was used as a base catalyst. To increase the efficiency of the reaction, ionic liquids and modified zirconia catalysts were used. A one-pot reaction of 2-acetylpyridine and pyridine carboxaldehyde in an ionic liquid medium was used to synthesize 47 (pyridyl) terpyridines. The aldol condensation and Michael addition were carried out sequentially at 100-140 o C and then the reaction performed a cyclization to produce terpyridine derivatives. Isolation of products was through filtration and washing with water to eliminate salts. In the catalytic research, sulfated zirconia (SZ), and borate zirconia (BZ) catalysts were synthesized and calcined at different temperatures (500850 o C). Powder X-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FT-IR) and BET surface area analysis were used to determine their structural properties. Solvents-free Claisen Schmidt condensation reactions under microwave radiation were used to test catalytic activity using cyclic ketones and aromatic aldehydes. Conditions of the reaction, such as the loading of catalysts, reaction temperature and time were optimized. When required, the products were recrystallized or chromatographed to purify them. Synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, gas chromatographymass spectrometry (GCMS), and elemental (CHNS) analysis. Yield (%) was measured, and the data were evaluated by comparative tables and graphical analysis to determine the efficiency and reproducibility.

Results

The 4-pyridyl-terpyridines synthesized were effectively characterized by spectroscopy and analysis. The ^{1}H NMR spectra displayed typical aromatic protons signals of 7.3-9.5 ppm indicating that heterocyclic structures of pyridine were formed. The ^{13}C NMR spectra also indicated the integrity of the structure with carbon peaks found between 117156ppm of the aromatic carbons.

Analysis of GC-MS always showed that there are molecular ion peaks at the m/z value of about 310, which confirms the molecular structure predicted. Close result of elemental (CHNS) analysis indicated high purity of synthesized compounds as there was agreement between calculated and experimental values. PXRD characterization of catalysts as in figure 1 revealed that the sulfated zirconia (SZ) heated at 650 C, was characterized by tetragonal phase which is known to have high catalytic activity.

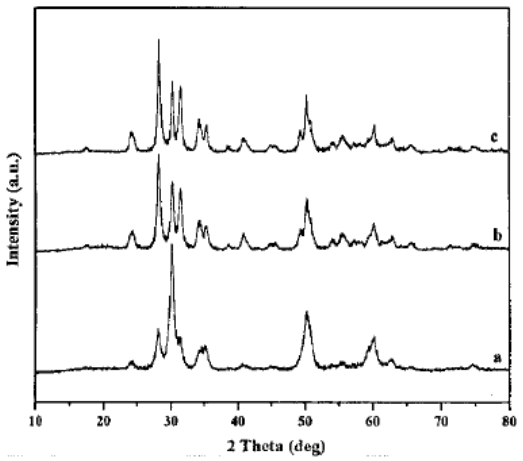

Figure 1: PXRD pattern of sulfated zirconia samples

At elevated calcination temperatures (750850 C), a slow conversion to the monoclinic form was noted, with a decrease in catalytic activity. FT-IR spectra were used to verify the presence of sulfate groups by typical bands in the range of 1200-900 cm -1. Analysis of the BET showed mesoporous structures with a large surface area. Likewise, borate zirconia (BZ) (shown in figure 2) catalysts exhibited stabilization of the tetragonal phase with borate-incorporation, and had better thermal stability than pure zirconia. FT-IR analysis identified borate species and the higher the boron loading the higher the catalytic activity.

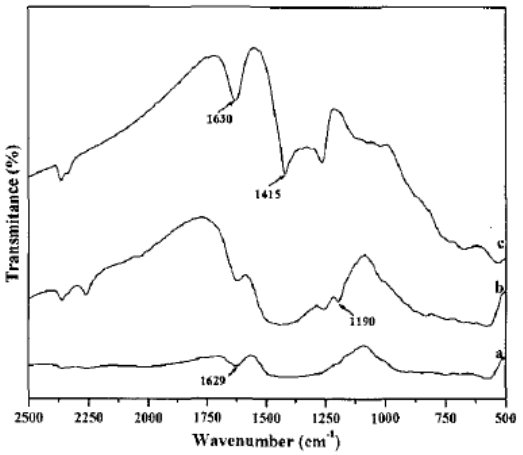

Figure 2. FT-IR spectrum of borate zirconia catalyst calcined at 650 cC: (a) 15 mol% BZ; (b) 30 mol% BZ; (c) recycled borate zirconia catalyst activated at 450 cc. Babou *et al.,* have attributed the bands at 768, 580 and 540 cm-I in the FT-IR spectra of the Zr02 correspondent to the crystalline zirconia.

The peaks accentuated around 1410, 1380 and 1193 cm-I corresponded to $[BO_3]^{3-}$ ions. Using solvent-free microwave catalytic studies, modified catalysts (SZ-2 and BZ) were shown to significantly enhance the yield of the reactions. Optimized catalyst loading enhanced the yield to between 70 and 95% with the catalyst. Peak productivity was attained at 650 -1 calcination temperature and ratios of catalyst to substrate of 1:5. The responses were filled in under 15-20 minutes, which is very efficient.

Discussion

The results clearly demonstrate that spectroscopic techniques effectively confirmed the successful synthesis and purity of terpyridine derivatives. The consistency between NMR, GC–MS, and elemental analysis indicates the reliability of the synthetic method. The observed chemical shifts and molecular ion peaks align well with expected structural features, validating the formation of the desired heterocyclic compounds [4]. Catalyst characterization highlights the critical role of crystalline phase and surface properties in determining catalytic performance. The dominance of the tetragonal phase in sulfated zirconia at 650 °C is a key factor contributing to enhanced activity, as this phase provides stronger acidity and better active sites. The decline in activity at higher temperatures can be attributed to the formation of the less active monoclinic phase [5]. The incorporation of sulfate and borate ions significantly improved catalyst efficiency by increasing surface acidity and stabilizing active phases. The superior performance of SZ-2 compared to SZ-1 further confirms that higher sulfate loading enhances catalytic activity. Similarly, borate-modified catalysts exhibited improved stability and reaction rates [6]. The catalytic reactions under microwave and solvent-free conditions demonstrated remarkable efficiency, reducing reaction time while achieving high yields. The absence of solvent not only supports green chemistry principles but also enhances reactant interaction, improving reaction kinetics. The consistent formation of bis-condensation products indicates high selectivity of the catalytic system [7], the study establishes a strong correlation between catalyst structure, surface chemistry, and catalytic performance, confirming that modified zirconia catalysts are highly effective for green synthetic applications.

Conclusion

The study demonstrates that ionic liquid-assisted synthesis combined with modified zirconia catalysts provides an efficient and sustainable route for heterocyclic compound production. High yields, reduced reaction time, and excellent catalytic performance under solvent-free conditions highlight its potential as a green and scalable alternative to conventional synthetic methodologies in organic chemistry.

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