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Research Article

Emeraldine Base Form of Polyaniline Nanofibers as New, Economical, Green, and Efficient Catalyst for Synthesis of *Z*-Aldoximes

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A facile, clean, economical, efficient, and green process was developed for the preparation of *Z*-aldoximes at room temperature under solvent-free condition using emeraldine base form of polyaniline as novel catalyst. In this methodology, PANI base absorbed the by-product of HCl (polluting chemical) from hydroxylamine hydrochloride and converted to polyaniline-hydrochloride salt (PANI-HCl salt). This PANI-HCl salt could be easily recovered and used in new attempts without any purification in many areas such as catalyst, electrical and electronics applications meant for conducting polymers. As far as our knowledge is concerned, emeraldine base as catalyst in organic synthesis for the first time.

1. Introduction

Oximes and their derivatives are important intermediates in the synthesis of amides [1–4], nitro compounds, hydroximinoyl chlorides, nitrones [5], amines, azoles, nitrile oxides, chiral α-sulfinyl oximes, nitriles [6–8], and isoxazolines [9].

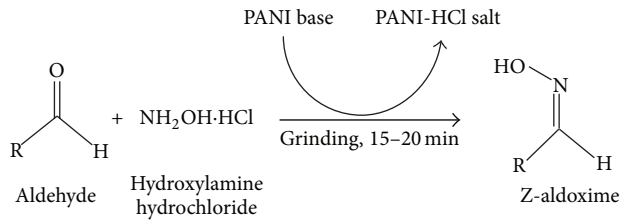
Both acids and general bases can act as catalysts for the preparation of oximes. A number of catalysts have been documented, such as TiO_2/SO_4^{-2} [10], ZnO [11], $CuSO_4$ and K_2CO_3 [12], glycine [13], CaO [14], silica gel [15], or without any base, but coupled with microwave irradiation [16], MW [17], K_2CO_3/MW [18], wet basic Al_2O_3/MW and molecular sieve 4 Å [19], NaOH [20], Ionic Liquid/water Biphasic System [21], silicaphos (P_2O_5/SiO_2) [22], and HPA [23]. Many methods are not very satisfactory due to drawbacks such as low yields, problems of generation of polluting HCl, high reaction temperature, long reaction time, and use of organic solvents.

Chemical methods for the synthesis of oximes usually give a mixture of two geometrical isomers (*Z* and *E*). A few methods are available for the synthesis of *E* and *Z* either isomer of oximes [12, 24]. In many cases, *E* isomers were obtained from the *Z* forms by hydrochloride method or purified by column chromatography [25]. Consequently, there is a need for developing an efficient, cheaper, convenient, and nonpolluting method for the preparation of stereoselective oximes.

In this work, *Z*-aldoximes in excellent yield in short reaction time were prepared from aldehydes with hydroxylamine hydrochloride under solvent-free condition at room temperature using emeraldine form of polyaniline base as novel polymer base catalyst. In this method, PANI base absorbed the by-product of HCl from hydroxylamine hydrochloride and converted to PANI-HCl salt, which is very much useful in various applications and makes the methodology towards the area of "Green Chemistry."

2. Experimental

2.1. Materials and Instrumentation. Aniline (reagent grade) from Merck was distilled before use; sodium persulfate, sodium hydroxide, hydroxylamine hydrochloride, and aromatic aldehydes are purchased from SD-Fine Chemicals, India, and were used without further purification unless otherwise noted. Powder of PANI samples was pressed into disk of 13 mm diameter and about 1.5 mm thickness under a pressure of 400 MPa. Resistance of the pellet was measured by two-probe method using digital multimeter 2010 (Keithley,



Scheme 1: Polyaniline base as catalyst in stereoselective synthesis of aldoximes.

Cleveland, Ohio, USA). FT-IR spectra of PANI samples were registered on a FT-IR spectrometer (Thermo Nicolet Nexus 670, USA) using the KBr pressed pellets technique. X-ray diffraction profiles for PANI powders were obtained on a Siemens/D-500 X-ray diffractometer, USA, using Cu Kα radiation, scan speed of 0.045°/min. Morphological studies of PANI powders were performed using Hitachi make (Japan) of field emission scanning electron microscope with field emission gun. The sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample from possible charging.

2.2. General Procedure for the Preparation of PANI Base. Polyaniline base was prepared by aqueous polymerization pathway by the reported procedure [26]. In a 250 mL round-bottomed flask, 60 mL of water was taken and 9.6 mL of HCl was added slowly with stirring. 1 mL of aniline was added to this mixture and the solution was kept under constant stirring at ambient temperature. 40 mL aqueous solution containing sodium persulfate (3.3 g) was added to this solution immediately. The reaction was allowed to continue for 4 h at ambient temperature (25–30°C). The precipitated polyaniline powder was filtered, washed with distilled water, and followed by acetone. Polyaniline salt synthesized above was stirred in 100 mL aqueous sodium hydroxide solution (1.0 M) for 4 h at ambient temperature. Polyaniline base powder was filtered, washed with excess water and finally with acetone, and dried at 50°C till a constant weight.

2.3. General Procedure for Preparation of Z-Aldoximes. In a typical reaction, a mixture of the aldehyde (1 mmol), hydroxylamine hydrochloride (1.2–1.5 mmol), and PANI base (100 mg) was grounded thoroughly in a mortar for 15–20 minutes. The mixture was washed with ethyl acetate and filtered to remove the catalyst. The filtrate was washed with water and brine solution and dried over anhydrous Na_2SO_4 followed by evaporation of solvent *in vacuo* to furnish the *Z*-aldoxime (Scheme 1). All the products were characterized by proton NMR and infrared spectra. The ^{1}H NMR and IR spectral results of the synthesized products are well matched with the same reported compound in the literature [12, 22, 23].

3. Results and Discussion

3.1. Polyaniline. Polyaniline (PANI) is the most important among all the conducting polymers due to its straight forward

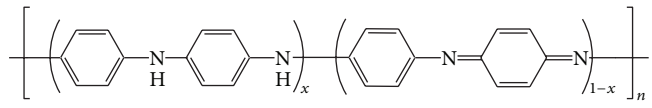


Figure 1: General structure of polyaniline base.

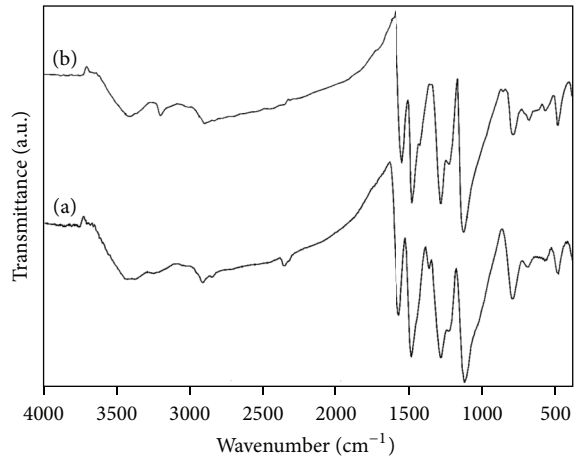


Figure 2: Infrared spectra of (a) PANI-base and (b) polyaniline sample recovered after the reaction.

polymerization, chemical stability, relatively high conductivity, redox properties, and cheaper and potential applications in various fields [27–30]. Usually, polyaniline is being synthesized from monomer aniline either by chemical or electrochemical polymerization process. Chemical polymerization process is more feasible route to produce large-scale PANI for the industrial use as compared to electrochemical polymerization.

The structure of polyaniline is known as a para-linked phenylene amine imine. The base form of polyaniline can, in principle, be described by the following general formula (Figure 1).

In the generalized base form $(1-x)$ measures the function of oxidized units. When $(1 - x) = 0$, the polymer has no such oxidized groups and is commonly known as a leucoemeraldine base. The fully oxidized form, $(1 - x) = 1$, is referred to as a pernigraniline base. The half-oxidized polymer, where the number of reduced units and oxidized units is equal, that is, $(1-x) = 0.5$, is of special importance and is termed as the emeraldine oxidation state or the emeraldine base form of polyaniline (PANI base). Partially oxidized emeraldine base is shown to be alternating copolymer of reduced and oxidized repeat units.

3.2. Catalyst Synthesis and Characterization. PANI base nanofibers were prepared directly by oxidizing aniline using sodium persulfate oxidant in the presence of hydrochloric acid, followed by dedoping the PANI-HCl salt to the polyaniline base (PANI). The infrared spectrum of PANI base (Figure 2(a)) showed major characteristic peaks at 3450, 2920, 2850,

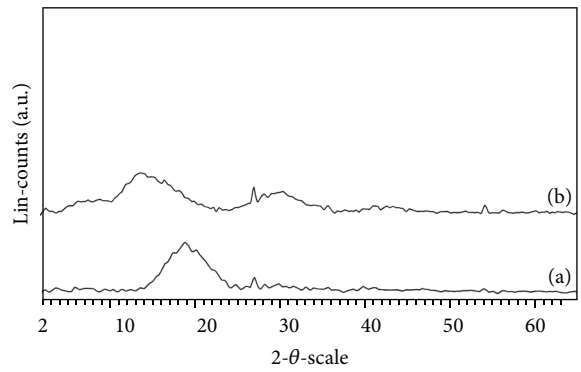
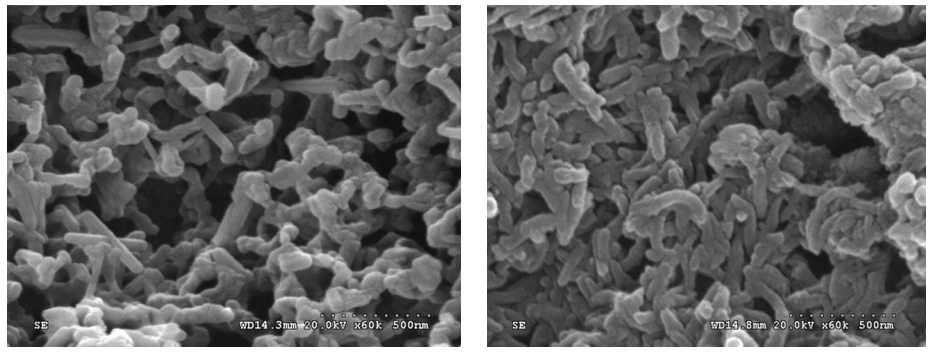


Figure 3: X-ray diffraction pattern of (a) PANI-base and (b) polyaniline sample recovered after the reaction.



(a) (b)

Figure 4: FE-SEM picture of (a) PANI-base and (b) polyaniline sample recovered after the reaction.

1580, 1495, 1375, 1295, 1210, 1135, and 810 cm^{-1}, which are similar to the standard PANI [31, 32]. The infrared spectrum of polyaniline sample recovered after the reaction showed major characteristic peaks at 3440, 2920, 1565, 1490, 1380, 1295, 1215, 1135 and 810 cm^{-1}, which are similar to those of PANI base. In addition to these peaks, a peak appeared at 3225 cm^{-1} (Figure 2(b)). This peak indicates that PANI base contains a dopant, that is, formation of PANI salt.

X-ray diffraction pattern of PANI base (Figure 3(a)) showed a broad peak around $2\theta = 19^{\circ}$, which is characteristic peak of polyaniline base. XRD pattern of polyaniline sample recovered after the reaction (Figure 3(b)) showed peaks at 30, 27, and 14° indicating the formation of emeraldine salt form of polyaniline [33, 34].

Morphological structures of polyaniline samples were found out from scanning electron microscopy. PANI base showed nanofibers with more or less uniform size (Figure 4(a)), and polyaniline sample recovered after the reaction also showed nanofiber (Figure 4(b)).

Conductivity of the polyaniline sample recovered after the reaction showed 0.01 S/cm, which is 10 orders of magnitude higher than that of PANI base (insulator level, $<10^{-12}$ S/cm). Increase in conductivity result confirms that insulating PANI base is converted to doped PANI salt. EDAX showed the presence of 9.5% of chlorine element. The above results indicate the presence of HCl as dopant on polyaniline salt; that is, PANI base absorbed HCl from hydroxylamine hydrochloride during the reaction with aldehydes and converted to PANI-HCl salt.

3.3. Polyaniline Base as Catalyst in Stereoselective Synthesis of Aldoximes. In our group, polyaniline salts are being used as polymer based solid acid catalyst in organic transformations [35]. In this work, for the first time, PANI base is used as polymer base catalyst in the preparation of stereoselective synthesis of aldoximes. Product was not obtained when benzaldehyde was ground with hydroxylamine hydrochloride in the absence of catalyst for 1 h. However, with the use of polyaniline base gave *Z*-benzaldoxime product (92% yield) in 20 min. (Table 1, Entry-1).

In order to check the versatility of the polyaniline base catalyst, various types of aldehydes were reacted with hydroxylamine hydrochloride using PANI and the results are included in Table 1. As shown in Table 1, the reaction of hydroxylamine hydrochloride with different aromatic aldehydes, including those with electron withdrawing and donating substituents in the presence of PANI base catalyst, gave aldoximes in good to excellent yields with *Z*-stereoselectivity without any side products. The *Z*-stereochemistry of the products was determined from the ^{1}H-chemical shift of the C(H)=N group which appeared around 8–8.5 as a singlet (Table 1).

Table 1: Conversion of aldehydes to *Z*-aldoximes using PANI base.

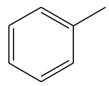
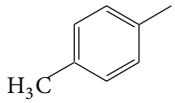
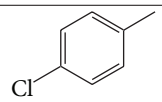
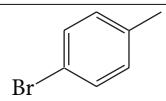
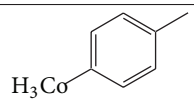
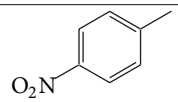
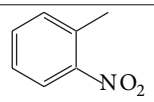
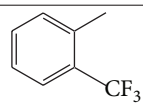
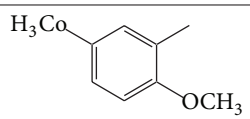
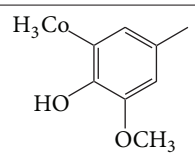
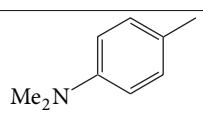
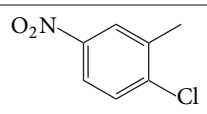
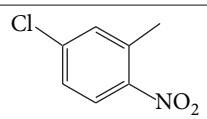
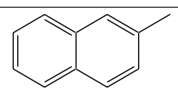
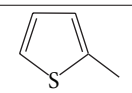
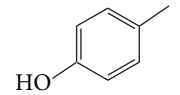
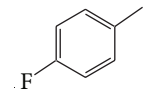
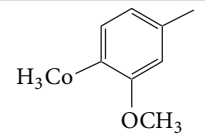
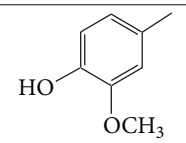
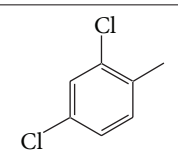
Entry	*Z*-aldoximes R	Isolated yield	^{1}H chemical shift of C(H)=N group
1		92	8.13
2		87	8.06
3		98.6	8.10
4		89	8.04
5		95	8.10
6		78	8.15
7		90	8.65
8		75	8.30
9		98.8	8.40
10		84	7.96
11		80	7.88
12		83	8.40
13		84.5	8.44
14		94	8.23

Table 1: Continued.

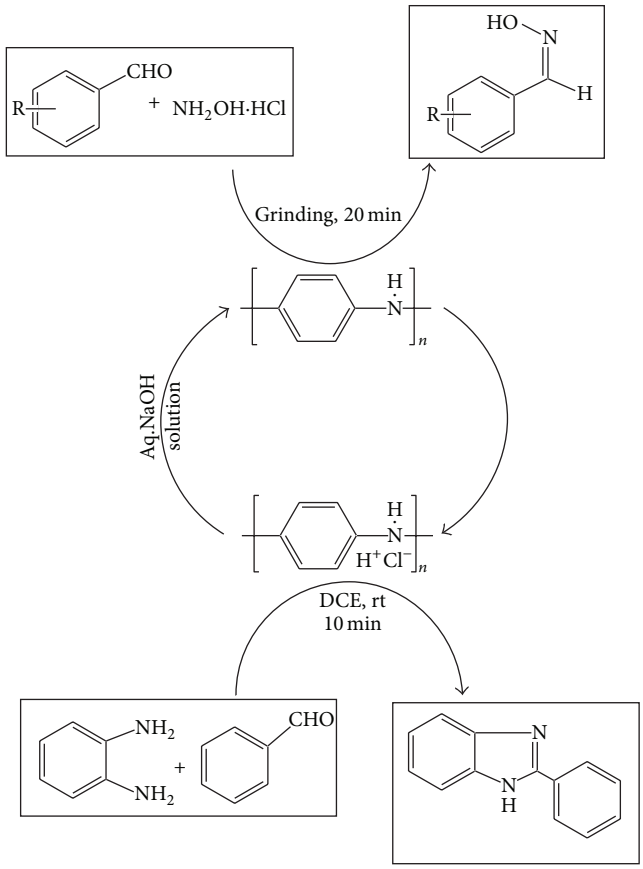
Entry	*Z*-aldoximes R	Isolated yield	^{1}H chemical shift of C(H)=N group
15		88	7.68
16		70	7.91
17		75	8.18
18		86	8.00
19		95	8.10
20		91	8.45

In a typical reaction, a mixture of benzaldehyde (5 mmol), hydroxylamine hydrochloride (6 mmol), and PANI base (500 mg) was ground thoroughly in a mortar for 20 minutes. The mixture was washed with ethyl acetate and filtered to remove the catalyst. Recovered catalyst after the reaction and polyaniline base were characterized by infrared, X-ray diffraction, EDAX, and conductivity measurements.

3.4. Use of Recovered Polyaniline-Hydrochloride Salt as Catalyst in Organic Reaction. In order to show the use of recovered PANI-HCl salt catalyst, the formed PANI-HCl salt was converted to PANI base by aqueous sodium hydroxide solution and again this PANI base was used as catalyst in the reaction of benzaldehyde with hydroxylamine hydrochloride to benzaldoxime (Scheme 2), which gave 91% yield. In addition, the formed PANI-HCl salt is tried out as polymer based solid acid catalyst in the synthesis of 2-phenyl benzimidazole (in 77% yield) from the reaction of o-phenylenediamine (1 mmol) and benzaldehyde (1 mmol) at room temperature in dichloroethane (5 mL) in 10 min. (Scheme 2). The PANI-HCl catalyst was reused for four more runs without significant decrease in activity.

4. Conclusions

In summary, good to excellent yields of stereoselective *Z*-aldoximes were prepared without any side products using



Scheme 2: Synthesis of aldoximes using PANI base, conversion of recovered PANI-HCl salt to PANI base and synthesis of 2-phenyl benzimidazole using recovered PANI-HCl salt.

only 1 : 1.2 ratio of reactants under solvent-free condition at room temperature with easily synthesizable, stable, easy, handlable, and usable catalyst by simple, clean, economical, and green process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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