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Microwave-Assisted and Green Synthesis of Schiff Bases Using Organic Red Clay as a Natural Acid Catalyst

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Abstract—**A new efficient and environmentally friendly procedure developed for the synthesis of Schiff base of aniline with aromatic aldehyde. The work involved the synthesis of 2 [(E)-(Phenylimino) methyl] phenol from salicyaldehyde & aniline and (E)-N-(4 Methoxybenzylidene)benzenamine from anisaldehyde & aniline in solvent-free condition under microwave irradiation. Organic red clay was employed as natural acid catalyst for the synthesis of Schiff base. Organic clay catalysts were characterized by EDX (Energy dispersion x-ray analysis), XRD (X-ray diffraction) techniques. Elemental composition of red clay was determined by EDX pattern recorded in the binding energy region of 1-10 KeV. The Schiff base thus synthesized from organic clay was characterized by FT-IR and NMR spectra techniques. This green synthetic approach found to have advantages like good yields, reduction in reaction time, exclusion of toxic organic solvents, operational simplicity.**

Index Terms—**Microwave irradiation, Schiff base, Solvent-free, Organic clay**

I. INTRODUCTION

Schiff bases play an important role in coordination chemistry as these organic compounds contains imines or azomethine groups. These compounds show variety of biological activities such as antifungal, antibacterial, antiviral, antipyretic, antimalarial, anti-inflammatory and antiproliferative properties. [1-3] Schiff bases are also used polymer stabilizer [4] and it is used in dyes, pigments and as catalyst in number of enzymatic reactions. The imine group which contains carbon nitrogen double bond (C=N) present in the schiff bases play significant role in biological system. Hence, schiff bases are most versatile class of compounds against microbes. [5] Among the different methods for synthesis of Schiff bases in which classical synthesis includes azeotropic distillation. [6] In 2004 Chakraborti et al. explained the function of bronsted- lowry acids to activate the carbonyl group of aldehydes for the synthesis of Schiff bases. [7] Till now many Bro¨nsted-Lowry or lewis acids used for the synthesis of Schiff bases includes According to literature survey many Bro¨nsted-Lowry or lewis acids used for the synthesis of imines while synthesizing Schiff bases include ZnCl2, TiCl4, MgSO4 PPTS, Ti(OR)4, alumina, H2SO4, NaHCO3, Er(OTf)3, P2O5/Al2O3, HCl. [8-18] Also, a number of new techniques have been reported including microwave irradiation, solid-state synthesis, water suspension medium, molecular sieves/infrared irradiation, infrared irradiation/no solvent, ultrasound irradiation. [19- 25] Silica gel supported sodium hydrogen sulfate and calcium oxide also used as heterogeneous catalyst for the synthesis of imines. [26, 27] In general, reported synthesis of schiff base involved drastic condition namely the use of Dean Stark apparatus, higher temperature, longer reaction time, tedious process. Among these new techniques microwave irradiation method is greener, efficient in terms of reaction rates, enhanced yields, easy work-up and is less environmentally problematic than other methods and follow ‘green chemistry’ protocols. Clay minerals as we know they have their rich history in medicine and ceramics, now they are emerging as potential catalyst. Organic clays when combines with microwave irradiation in solvent-free conditions provides greener process which is less costly, selective, eco-friendly. [28] Organic clays catalyzes broad variety of chemical transformation [29] because due to their physical nature clay as a catalyst absorbs microwave energy and it becomes excellent catalyst for microwave-assisted organic synthesis [30]. When the compounds are adsorbed on the surface of the catalysts reactions are significantly more rapid than in solvents. Studies to scale up the microwave-assisted reactions from the laboratory to industrial scale without changing the laboratory optimized reaction conditions have been investigated.

II. RESULT AND DISCUSSION

Typical EDX spectra recorded for organic red clay are shown in Fig. 1. Results are summerised in Table 1 [Supporting information]. The elements present in the mineral structure are partially responsible for the catalytic activities of clays. From the EDX spectra it was cleared that organic red clay contains Oxygen (O), Aluminium (Al), Silicon (Si), Iron (Fe) elements in large percentage as compared to other elements. (Main Element Composition). According to EDX Spectral data, the sample contains oxygen (O), Sodium (Na), Magnesium (Mg), Aluminium (Al), Silicon (Si), Potassium (K), Titanium (Ti), Iron (Fe). Organic clay which is used as catalyst may and usually will have different catalytic activity for distinct reactions.

Compound	Organic Red Clay			
	Time (min)	Power (w)	M.P. (˚C)	% Yield
AS	5	400	52˚C	81
AA	6	400	50˚C	80

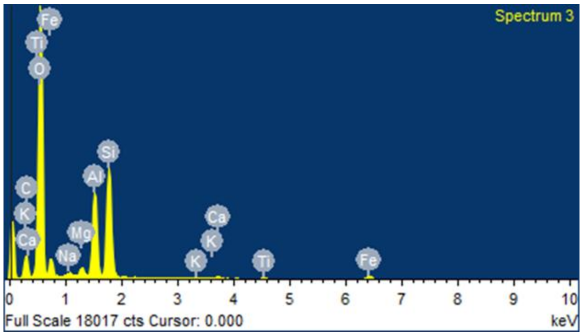


Fig. 1 EDX spectra of Red Clay

Component of clay and clay size play important role in mechanism of catalytic activities. High surface area, chemical nature, low dimensionality, and increase local concentration of reactants these are the size effects caused by size of the clay. The surfaces of the clay particles were examined with a scanning electron microscope (SEM), coupled with an energy dispersive x-ray spectroscopy (EDX). Clay soil is composed of millions of clay particles which are 0.002 mm in diameter or smaller. We have calculated the 2θ and crystallite size of the red organic clays from the XRD spectra which are shown in Fig. 2. Results are summarised in Table II.

Table II: XRD spectral analysis of red clay

Clay	2θ	Crystallite Size (nm)
Red Clay	48.783	20.407

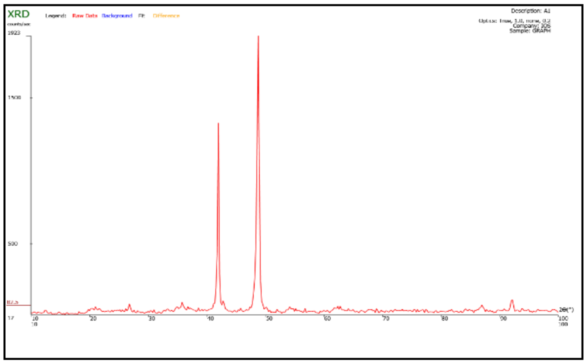
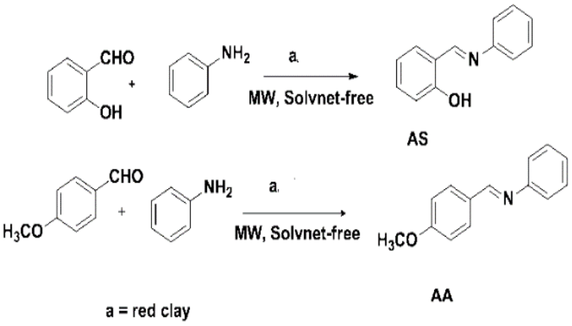


Fig. 2 XRD Spectra of Red clay

Table III: Microwave assisted solvent-free organic clay catalyse synthesis of Schiff base

From the Table III, it is cleared that 2-[(E)-(Phenylimino) methyl] phenol (AS) and (E)-N-(4 Methoxybenzylidene)benzenamine (AA) were successfully obtained by using red organic clay as acid catalyst under microwave irradiation in solvent-free condition. On comparing the progress of reaction, best yields were obtained at 400 W. It was observed that best yield was obtained with red clay (0.5 g) for N-salicylidene aniline2-[(E)-(Phenylimino) methyl] phenol (81%) and for (E)-N-(4-Methoxybenzylidene) benzenamine (80%). From the EDX analysis it is observed that iron content is more in red clay. From the XRD spectral analysis it is cleared that crystallite size of red clay was approximately 20 nm.



Scheme 1

Clays are the aluminosilicates with layered structures, they provide several possibilities for synthetic applications and can be used as acid or base catalysts for various types of organic reactions [31]. Novel green method using organic clay for the synthesis of Schiff base has been established. To obtain the Schiff base it is necessary to pay attention to the factors, such as choice of catalyst and appropriate pH range. Acidic nature of the clay causes the structural characteristics which imparts activity. First we tested the pH of organic clay which is used for experiments because formation of Schiff base is pH – dependent reaction. It has been observed that the pH of red clay was found to be 3.6 which is required for Schiff base synthesis because optimal pH is between pH 3-4 which is suitable for starting nucleophilic addition reaction and performing elimination reaction at sufficient speed [32]. Here organic red clay act as mild lewis acid catalyst which accelerates nucleophilic attack of amines on carbonyl carbon as well as serving as dehydrating agent for removal of water in second step under solvent-free condition by using microwave irradiation. In mechanism clay minerals act as mild acid catalyst, facilitates the protonation of carbonyl oxygen and accelerate the nucleophilic attack. The clay's surfaces can adsorb both amines and carbonyl compound, brings them into close proximity and increases the reaction rates. The porous structure of clay can help to remove water formed during the reaction, shifts the equilibrium towards the formation of Schiff base. We felt the need to develop a methodology for synthesis of Schiff base under microwave irradiation using organic red clay as natural acid catalyst for the first time ever.

III. MATERIALS AND METHODS

Reactions were monitored by thin layer chromatography on 0.2 mm silica gel F-252 (Merck) plates. All the chemicals and reagents used were of analytical grade. Organic red clay was collected near Panvel region. These organic clay purified via simple washing and analysed by EDX, XRD characterisation techniques. To check the pH of clay Digital Equiptronics (Model EQ - 610) pH meter was used. Melting points were recorded by an open glass capillary sealed at one end melting point tube and are uncorrected. Crude product was recrystallized from hot ethanol to get pure product. Infrared spectral studies were carried out using KBr discs on a Perkin Elmer FTIR/4000 spectrophotometer. ^{1}H NMR and ^{13}C spectra were recorded in DMSO-d6 on Bruker Advance II 400 NMR spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR are reported in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard in CDCl$_3$/DMSO-d6 as a solvent. All Schiff bases are known and their spectral data matches with reported literature values [33].

General procedure for the synthesis of schiff base: A mixture of salisaldehyde/anisaldehyde (0.01 mol), aniline (0.01) and 0.5 g organic red clay were added in beaker. The contents were subjected to microwave irradiation at 400 W for about 3-7 min. Progress of the reaction was monitored by TLC Hexane: Ethyl acetate (7:3). After the completion of the reaction (as followed by TLC), the product was extracted in 80% EtOH. After filtration spent catalysts were collected. The crude product thus obtained was recrystallized from EtOH to afford desired product in pure form.

2-[(*E*)-(Phenylimino)methyl]phenol: (AS) FTIR: 3064.42 cm^{-1} for aromatic −OH stretching, 2886.47 cm^{-1} for aromatic −C−H stretching, 1682.11 and 1616.42 cm−1 for −N_CH− stretching, 1484.53 cm−1 for Ar−C_C− stretching.

^{1}H NMR δ 7.35 (m, 5H), δ 8.65 (s, 1H), δ 6.76 (d, 1H), δ 7.12 (dd, 1H), δ 6.85 (dd, 1H), δ 7.45 (d, 1H).

^{13}C NMR δ 119.07, δ 153.2, δ 130.1, δ 127.3, δ 160.1, δ 118.5, δ 132.28, δ 161.13, δ 162.68, δ 116.0, δ 132.5, δ 121.5, δ 130.6.

(*E*)-*N*-(4-Methoxybenzylidene)benzenamine: (AA**)** FTIR: 3050.49 and 2962.28 cm−1 for aromatic −C−H stretching, 2880.32 cm−1 for aliphatic −C−H stretching, 1684.32 and 1621.28 cm−1 for −N_CH− stretching, 1573.88 and 1507.88 cm−1 for Ar−C_C− stretching, 1073.49 and 1030.43 cm−1 for −C−O−C ether linkage. 1H NMR δ 7.37 (m, 5H), δ 8.39 (s, 1H), δ 7.42 (d, 2H), δ 6.98 (d, 2H), δ 3.87 (s, 3H). 13C NMR δ 120.9, δ 130.5, δ 125.5, δ 152.3, δ 159.7, δ 126.1, δ 130.2, 114.2, δ 162.2, δ 55.43.

pH of Organic Clay: Weighed separately the 10g of red clay into the beaker. Added 50 ml of distilled water to the beaker containing clay. The ratio taken is 1:5 for clay: water. Stirred the beakers for about 2-3 min then allowed the clay to settle for 2 minutes. Measured the pH value of the water above the clay in the beaker by using pH meter.

Characterisation of Organic Clay: Elemental composition of organic clay determined by EDX pattern recorded in the binding energy region of 1-10 KeV was shown in **Fig. 1**. Results are summarised in **Table I**.X-ray diffraction (XRD) pattern of organic clay was recorded using an X-ray Diffractometer (Rigaku; model Miniflex –II) with monochromatic Cu K-α radiation (λ = 1.54178 A°) is shown in **Fig. 2.** The XRD data was collected with a scan rate of 3° per minute. Energy dispersive x-ray analyser (EDXA), Oxford instrument was used in conjuction with SEM (Scanning Electron Microscope) model JEOL JSM-6010 to measure the elemental composition of clay. From XRD pattern, crystallite size of the organic clay is calculated by using Debye-Scherrer equation. Results are summarised in Table

IV. CONCLUSION

In conclusion, we have described a green & efficient new method for the synthesis of Schiff base by using organic red clay as natural acid catalyst. pH was determined by pH meter was found to be 3.6. Crystallized size was calculated from XRD analysis of red clay was found to be 20 nm. We have successfully employed organic red clay as natural acid catalyst.

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