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Microwave Assisted Modification of Bentonite Clay: Characterization and Solvent Free Synthesis of Schiff's Bases

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Abstract

The acid modified bentonite catalysts prepared from bentonite clay activated under microwave irradiation with different concentrations of H_2SO_4 (0.1, 1, 2 and 3M). A series of novel and significant compounds containing Schiff's base substituted aromatic compounds have been synthesized using modified clay in solvent-free conditions under microwave irradiation. The structures of obtained compounds were analyzed by H-NMR, FT-IR spectral studies and the prepared heterogeneous acid activated catalysts were characterized by PXRD, SEM, BET, FT-IR and UV-Visible spectral analysis. PXRD studies showed the phases of catalyst and average crystallite size is analyzed in the range of 11-18 nm. The optical properties of the catalysts were investigated by UV–Vis; demonstrate the energy band gap of the catalyst. This modified clay catalysts can be re-used up to 3-4 times and further used in practical applications.

Keywords: Solvent free-microwave synthesis; Schiff's base; Acid activated clay

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Introduction

Green chemistry furnishes a use of alternative reagents, catalysts with solvent free, replacement of the conventional with greener ones and development of clean chemical synthesis [1]. Homogeneous catalysts are more expensive and serious environmental issues associated with product separation, purification, corrosion and waste generation attract great efforts toward the development of processes mediated by heterogeneous catalysts, therefore we used newly prepared solid heterogeneous modified clay catalysts for organic reactions [2,3]. Heterogeneous catalysts are more sustainable and alternative renewable catalyst for the production of organic compounds owing to environmental concerns. Bentonite is a mineral, extensively used for different applications and expressed as hydrated aluminosilicate. The compositions of Bentonite clay consists 85% of montrorillonite and the additional components are: quartz, feldspar, gypsum and other minerals [4]. Bentonite clays are used as an efficient solid acid catalyst for a number of organic and liquid-phase reactions and offer several advantages over classic acids: strong acidity, non-corrosives, cheapness, mild reaction conditions, high yield and selectivity, ease of set up and work up [5-7]. Bentonite clay materials are heterogeneous solid clay and it can be modified by treating with acids, which involves the removal of different ions plugging the surface pores, by formation of surface pores and cracks with decrease in size resulting to increased surface area and pore volume [8]. During the acid modification of clays, the ion exchange of aluminum in the octahedral layer can be leached out by Na, K, Fe, Mg, Zn, Ni, Li etc., ions and results in the alteration of parameters forms porosity and increases in catalytic properties [9]. Which are not only eco-friendly but also be easily operating and available in huge quantities at very cheap price. Modification of clay is an important process, which involves changing physical and chemical properties of clays [4]. Acid activation of clay catalysts were achieved by microwave heat treatment in short period of time. Microwave irradiation of reactant and solvent mixtures are quickly activated by a heat source, its adequate supply of heat leads to increasing the transferring energy into the reaction mixture and increase the rate of reaction compared to conventional heating [10,11]. Microwave irradiation shows high activity with short duration, due to activate the molecules in mixture by microwaves coupling directly, leading to a rapid rise in temperature and completing the reaction [4]. This is attributed to sustainable, reduction of pollution, new ways for environmentally friendly reactions, thermally inert, environmental friendly and recycled for about 2-4 times [3].

The Schiff bases have attracted notable aspects due to their significant in industrial applications, ligands synthesis [12], organic synthesis [13] and its biological activities such as antibacterial, antifungal [14], antitumor, antiviral, anti-HIV, antiproliferative, herbicidal and anti-influenza A virus activities [15-17]. Schiff base syntheses are attractive under microwave irradiation with solvent free conditions using heterogeneous modified acid activated clay catalyst. Synthesis by condensation of primary amine (aniline) with aromatic aldehyde leads to the formation of C–N double bond and it essential have been found to posses more inhibitor efficiency than their constituent carbonyls and amines [18]. A recent work in the Schiff base synthesis with various catalysts leads to implementation of product yields under microwave treatment [19-21]. Different groups of catalysts or solid acids have been found active in the chemical reactions, including Montmorillonite clay was used as efficient solid acid catalysts for a number of organic and liquid phase reactions and offer several advantages over classic acids, alkali exchanged zeolites, ion-exchange resins, some environmental-friendly synthesis [16] etc.

In present work, we prepared heterogeneous acid modified clay catalysts by treating Bentonite clay with sulphuric acid and their catalytic activity has been studied over the Schiff's base synthesis under solvent free condition using microwave irradiation. The prepared acid modified clay catalysts and final organic products were analyzed by XRD, SEM, FT-IR, UV-Vis absorbance spectra, BET techniques AND HNMR and FT-IR spectroscopy respectively.

Experiment

Chemicals and catalyst

The reagents were used in experiment is aniline, benzaldehyde, salicylaldehyde and dimethylamino benzaldehyde. All the chemicals used in the present investigation were purchased from S. D. Fine Chemicals, Bombay, India and were used without further purification.

Clay modification

The microwave assisted synthesis of acid activated Bentonite clay catalyst by treating with H_2SO_4 showed surface and acidity modification. The modified clay catalysts were prepared from treating 10 g of clay with sequence of different concentrations of 500 ml H_2SO_4 (0.1M, 1M, 2M and 3M) in round bottom flask. The reactants mixture was transferred to the microwave reactor and microwave irradiation for 30 min at 338 K, whereas 24 h heating required in conventional heating method. Further, it allowed to settle down and washed with water until it is free from chloride ions. The obtained product was dried at 373 K for 3 h and well grinded to get a fine powder before subjected to characterization.

Characterization

The modified bentonite catalysts with different concentrations were well characterized using Shimadzu Powder X-ray diffractometer (PXRD) with Cu Kα (1.541 Å) radiation with nickel filter in the 2 θ range 20 - 70°C at a scan rate of 2°C min^{-1}. Acidity of modified clays was measured by FT-IR spectroscopy using pyridine as probe molecule. FT-IR spectra of the samples were then recorded in the range 4000-500 cm^{-1} using Bruker model Alpha-P IR spectrophotometer having resolution of 4 cm^{-1} fitted with a diamond ATR cell. The surface area was obtained by Brunner-Emmet-Teller (BET) method and the nitrogen adsorption–desorption isotherms were carried out using Quanta Chrome Nova-1000 surface analyzer at liquid nitrogen temperature. The UV-Visible studies of the samples were performed in the range 200-800 nm using Shimadzu UV-2600.

Results and Discussion

Characterizations of synthesized acid modified clay catalysts

PXRD analysis: Powder X-ray diffraction (PXRD) studies showed the determination of crystallinity and phase composition of prepared acid modified Bentonite clay catalysts by microwave irradiation as shown in **Figure 1.** The PXRD peaks indexed as (110), (130), (200) and (060) were well coordinated with card number 1985 [22]. Bentonite clay catalysts samples consisted of predominantly montmorillonite, substantial amounts of quartz, feldspar and gypsum impurities. During the modification of clay catalyst gives the ion exchange reaction with sulphuric acid in the octahedral layer of clay samples and leads to variation of parameters forms porosity and increases in catalytic properties. These maximums inter-allocation ions were observed in case of 2M H_2SO_4 catalyst, which involves changing physicochemical properties of clays specifically the surface pores with decrease in size resulting to increased surface area and pore volume under microwave treatment [23]. Thus, the crystallization process proceeds along (110) crystal plane and intensity of the plane that was found to be maximum for 2M compared to 0.1M, 1M and 3M H_2SO_4 activated clay. The crystallite sizes were estimated by Scherer's method [24,25] and results found to be in the range 12 to 18 nm for different concentrations of H_2SO_4 synthesized from microwave heating.

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where β (FWHM in radian), ε; the strain developed and D; the crystallite size.

IR analysis: Figure 2 show the FTIR spectral study (in the range, 4000–500 cm^{-1}) indicates in the identification of various functional groups present in the acid activated Bentonite clay with different

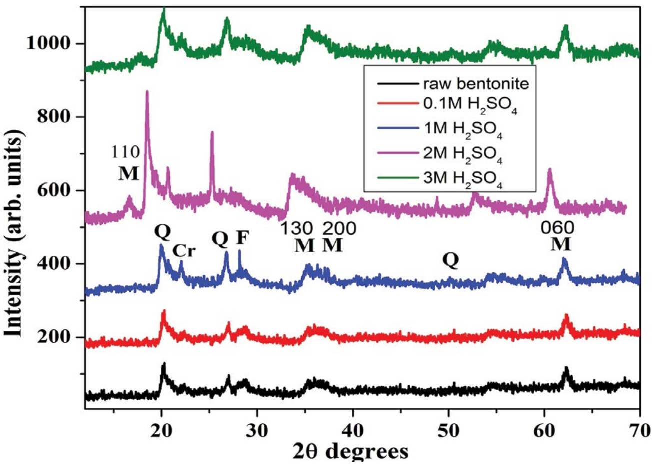


Figure 1 The PXRD patterns of the raw bentonite and acid activated Bentonite samples.

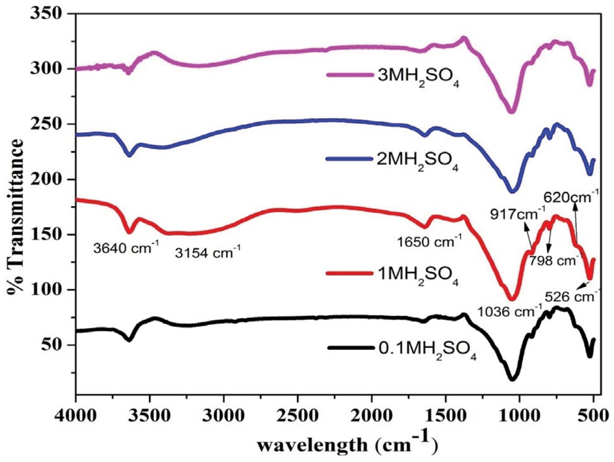


Figure 2 FT–IR spectra of the acid activated Bentonite clay catalysts.

concentrations (0.1M, 1M, 2M, 3M H^+). The Si-O stretching vibrations were observed at 798 cm^{-1}, 620 cm^{-1}, and 526 cm^{-1} showing the presence of quartz. The strong absorption bands at ~ 1100 - 1000 cm^{-1} and the most intensive band at 1036 cm^{-1} is attributed to Si-O stretching. A strong band at 3640 cm^{-1}, 3154 cm^{-1} indicates the possibility of the hydroxyl linkage and a band at 3624 cm^{-1} representing the stretching vibration of the hydroxyl groups of montmorillonite coordinated to octahedral Al^{3+} cations [26]. The inter layer hydrogen bonding in clay is assigned by a characteristics band at 3638 cm^{-1}. The bands at 917 and 798 cm^{-1} corresponding with the AlAlOH and AlMgOH bending vibrations were observed respectively. The band 620 cm^{-1} was indicate M-O vibrations, to the couple Al-O and Si-O stretching frequencies [27,28].

SEM analysis: The SEM micrographs of acid modified Bentonite clay catalysts prepared by microwave heating method at different magnification were show in **Figure 3.** In microwave heating method, heat energy plays a vital role in the preparing modified clay catalysts by a simple and quick synthesis route. Thus, the acid allocation into the Bentonite clays interior followed by the substitute of ions, forming a dense collection of acid activated clay [29]. After the modification of clay, the surface seems to be distressed by the grinding process and acid activation process [30]. This is reliable with the increase in surface area after the acid allocation into the material.

BET analysis: The surface area, porosity and textural properties of the synthesized modified clay and untreated raw Bentonite particle has been determined by BET method using liquid nitrogen (77 K) as adsorbent gas **(Figure 4).** The surface area is one of the important parameters to characterize powder samples related with other parameters such as particle size, shape, surface textures, size distribution, density and open porosity with in agglomerated particles [4]. The microwave heating derived products usually have a large surface area due to liberation of heat (exothermicity). During microwave reaction, the temperature is just enough to form nuclei but too short for grain growth. The increase in the surface area and pore volume is evidence for the increase in the strength of an acid. The increase in concentration of H_2SO_4 is attributed the presence of acid in between the layers of clay structure, due to incidence of the dealumination process and thus surface degeneration.

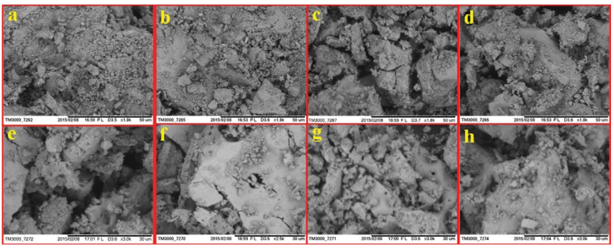


Figure 3 SEM images of 0.1M H_2SO_4 (a and e), 1M H_2SO_4 (b and f), 2M H_2SO_4 (c and g) and 3M H_2SO_4 (d and h) modified clays at different magnification.

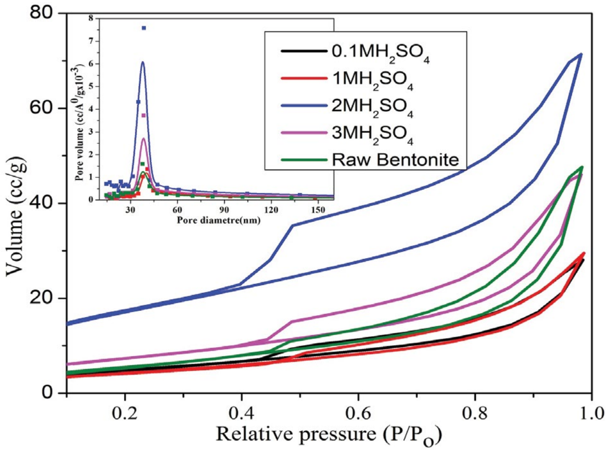


Figure 4 Nitrogen adsorption and desorption isotherms and pore volume distribution curve (inset) of Raw Bentonite and acid activated Bentonite.

The BET surface area and average pore diameter of acid treated (0.1M, 1M, 2M, 3M) and untreated raw Bentonite samples were found to be 16.21, 18.21, 60.40, 30.28 and 21.10 m^2/g) and (98.40, 86.04, 71.21, 2 86.31 and 133.13 Å) respectively. The large surface area and porous nature of the prepared samples were due to uniform distribution of particle as observed in SEM images.

Band gap analysis: The optical properties are very significant to select the materials for its specific applications. Therefore, the band gap energy (E_g) of the untreated Bentonite clay and (0.1-3M) H^+ treated Bentonite clay were evaluated. **Figure 5a** shows the UV-Visible absorption spectra of raw Bentonite clay and (0.1-3M) H^+ treated Bentonite clay powder samples. It was well recognized that have large surface to volume ratio that results in the formation of voids on the surface as well inside the agglomerated particles. Such voids can cause fundamental absorption bands in the UV region. All the samples exhibit a representative absorption with intense transition in visible region of the spectra that was due to the band gap transition of Bentonite clay and (0.1-3M) H^+ treated Bentonite clay. The band gap (E_g) of material can be calculated from the following relation.

$$Ah\gamma = A\left(h\gamma - E_g\right)^n$$

where hγ; photon energy, α; the absorption coefficient, A;

constant for the material and n; constant for transition [25]. The estimated direct E_g of the treated and untreated Bentonite clay with acid (H^+) was found to be 4.71 and 5.09 eV respectively. The constant associated to the different types of electronic transitions k=1/2, 2, 3/2, 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions respectively. The E_g values are predicted by extrapolating the linear portion of the curve in the UV–Vis absorbance spectra and further analysis of the present data showed that the plots of $[F(R)]^2$against energy give linear relations, which are most fitted for the above equation with k=2 for both untreated and treated Bentonite clay with acid (H^+) samples and their values are found to be in the range 4.71 and 5.09 eV. This indicates that the allowed direct transition is responsible for the interband transitions in untreated and treated Bentonite clay with acid (H^+) samples. The estimated direct E_g of the 0.1-3M H^+ modified Bentonite clay were found to be 5.56, 5.13, 4.61 and 4.71 respectively as shown in **Figure 5b.** It was interesting to note that the band edge of Bentonite clay and (0.1-3M) H^+ treated Bentonite clay have shifted towards higher energy side indicating blue shift.

The absorption band ranges from 200-500 nm was attributed to the surface state of Bentonite clay. The energy band gap of the material plays a crucial role in deciding the catalytic activity under microwave irradiation which participates in determining the e^-/h^+ recombination rate. From the data, it is clear that the blue shift in the band gap of acid treated Bentonite clay prepared using Bentonite clay with different concentration of H_2SO_4, it was due to quantum confinement effect since the crystallite size was less for 2M H_2SO_4 when compared to 0.1M, 1M & 2M H_2SO_4. The absorption in case of 2M H_2SO_4 was useful efficient catalyst to acid mediated reactions for Schiff's base synthesis through condensation reactions.

Synthesis of Organic Compounds

Atom economy

Atom economy is derived from the green chemistry principles and the most sustainable development perspective need to measure a particular reaction with maximum amount of all the raw materials ends up in the product and a minimum amount of waste is produced. Now a day's design the reactions with the uppermost possible atom economy in order to minimise green impact.

$$Atom\,economy = \frac{Molecular\,mass\,of\,desired\,product}{Molecular\,mass\,of\,all\,reactants} \times 100\%$$

The atom economy for the synthesis of Schiff's bases from Aniline with Aromatic-aldehydes over acid activated clays under solvent free condition shows the reaction route has 90.95% for N-[(E)-phenylmethylidene] aniline, 91.62% for 2-[(E)-(phenylimino) methyl]phenol, and 92.56% for N,N-dimethyl-4-[(E) (phenylimino) methyl]aniline and remaining percentage is waste product (H_2O).

Effect of parameters

We are optimized the reaction conditions by testing various parameters like effect of catalyst amount, reaction temperature, mole ratio of the reactants and reaction time for imination of Aniline with Aromatic-aldehydes over acid activated clays. Under optimum conditions, higher the product yield was achieved in the Schiff base synthesis of aniline with different Aromatic-aldehydes under microwave treatment. However, the variation of amount of catalyst influences the alteration in product yield. Thus, increasing in the conversion of aldehydes were achieved with the varying the catalyst amount from 0.1 to 0.7 g and the maximum conversion observed at 0.5 g due to availability of sufficient number of acid sites **(Figure 6A).** The molar ratio of reaction mixtures was changed from 1:1 to 1:3 in presence of 0.5 g of clay catalyst and 95 % conversion of Aldehydes were observed at the mole ratio 1:1 **(Figure 6B).** Temperature and reaction time has a significant effect on the chemical synthesis, higher the aldehydes conversion proceeds at 338 K and 150 secs respectively as shown in the **Figure 6C and 6D.**

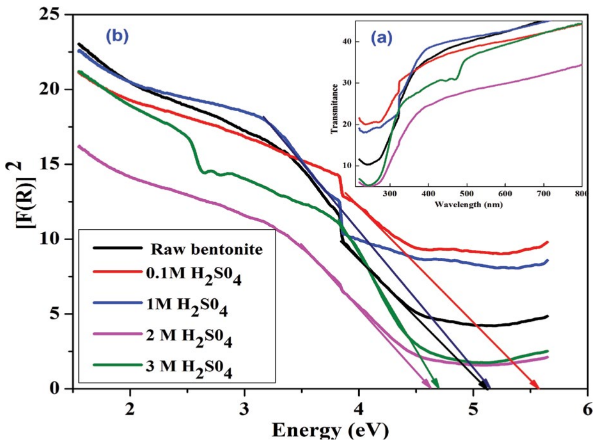
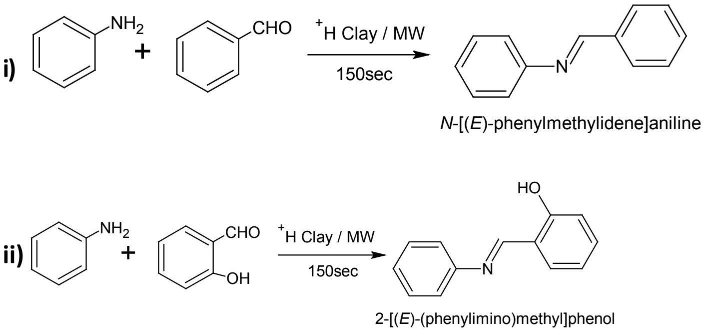


Figure 5 Optical absorption spectra **(a)** and Plot of $[F(R)]^2$ and energy (eV) of activated Bentonite material **(b)**.

Schiff base synthesis

Under optimized conditions, microwave irradiation of 5 m mol of aniline and 5 m mol of aromatic aldehydes were mixed with 0.5 g of acid modified clay catalyst in a microwave reactor. Microwave irradiation of reaction mixture for about 150 sec in the modified microwave oven and the obtained solid product was washed with cold water, recrystalized using ethanol. The percentages of Schiff's bases obtained under microwave heating in presence of acid modified catalyst are shown in **Table 1.** Based on all the above facts following reactions have been visualized to predict the most probable reaction mechanism as given in **Scheme 1.**

Reactions: Microwave assisted solvent free Acid Catalyzed Condensation reaction.



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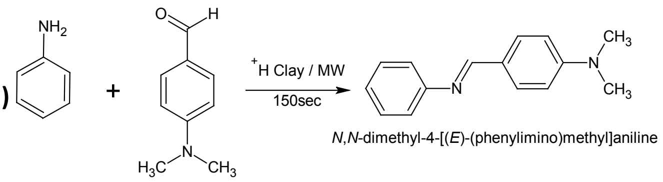


Spectral analysis of Schiff bases

Reaction of aniline with aromatic aldehydes takes place in three steps first through protonation of aldehydes, secondly, direct attack of aniline to electron deficient carbon in carbonyl group of aldehydes followed by elimination of water to form Schiff base product. FT-IR spectra for Schiff base compound was analyzed, **Figure 7** indicates that the bands at 1626-1591 cm^{-1} due to the C-C double bond and the presence of C=N functional group confirmed by the characteristic band stretching at 3059-1600 cm^{-1} [31]. The band at 3028 cm^{-1} due to =C-H stretching vibrations and the bending vibration band at 694-761 cm^{-1} showing that mono substituted benzene. The HNMR spectral analysis showed that appearance of single peak at 8.7 ppm, due to presence of proton in -CH=N- group. The protons in aromatic compounds appeared as multiple peaks within the range 6.9-7.8 ppm [32].

Catalyst deactivation

From the microwave heating, observed that higher catalytic activity and selectivity with shorter reaction times compared to the conventional heating. Compare to MW, Maximum yield of the products was not achieved in case of conventional heating after the recovery of the catalyst. The acidity of modified Bentonite clay samples were confirmed by treating the catalyst with pyridine and analyzed under FT-IR spectra. The absorption bands at 1441, 1488, 1547 and 1592 cm^{-1}, recognized to pyridine hydrogen bonded formed from acid reacts with clay material [33]. After the reactions, recovered clay catalysts are washed with toluene, and then dried in hot air oven for 3 h at 393 K. These catalysts were again reused in the reactions between aniline and Aromatic-aldehydes under optimized conditions in the microwave as well as conventional heating. Pyridine-FT-IR spectra of modified clays are shown in **Figure 8.**

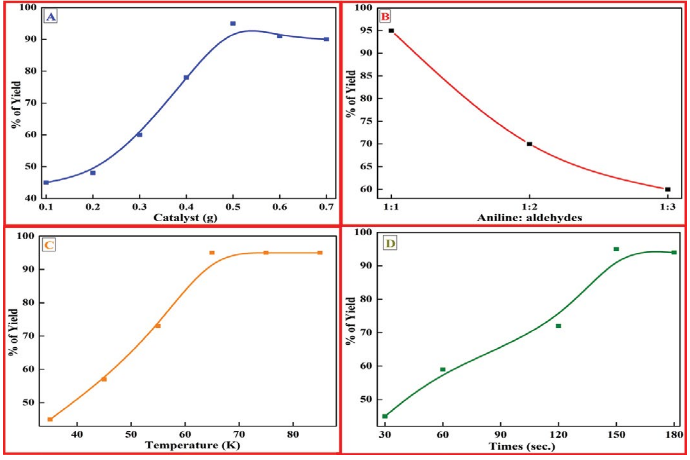


Figure 6 Reactions with various parameters like effect of (A) catalyst amount, (B) mole ratio (C) temperature and (D) reaction time for the imination of aniline with aldehydes.

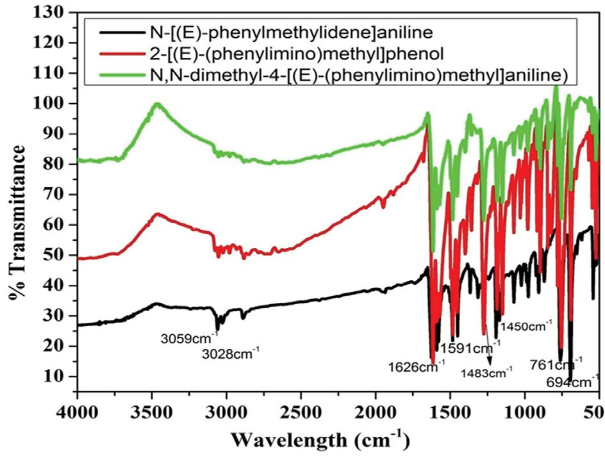


Figure 7 FT–IR spectra of the Schiff's base from aniline with benzaldehyde, salicylaldehyde and dimethylaminobenzaldehyde.

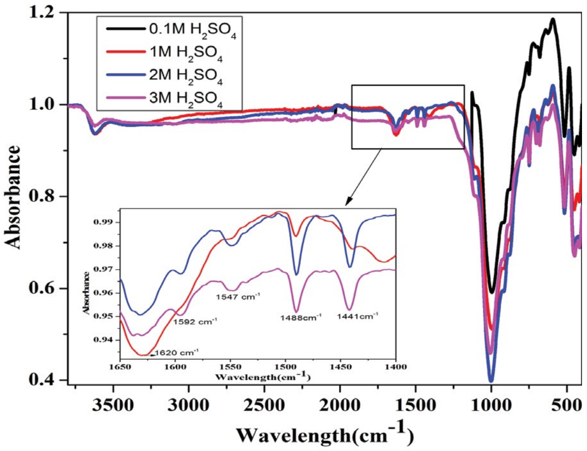
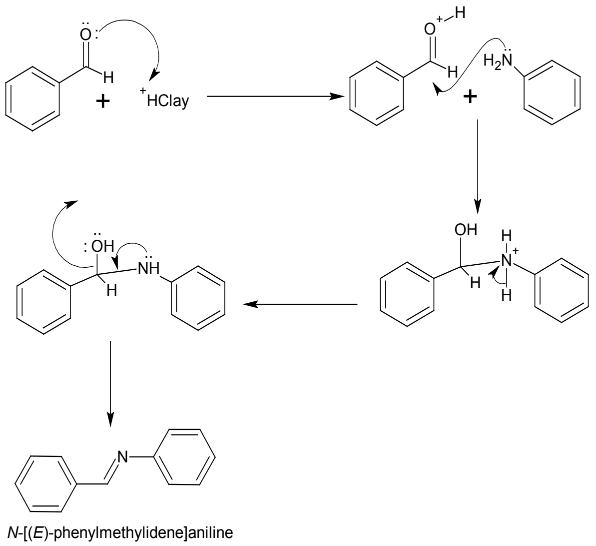


Figure 8 FT–IR spectra for acidity of acid activated Bentonite clay catalysts after the recycling.



Scheme 1 Reaction mechanism with catalyst for the imination of aniline with aromatic aldehydes.

Table 1 Percentage yield of Schiff's bases synthesized in presence of H^+ activated clay catalyst.

Catalyst	Conc. of Clay	Substrate	% Yield of imines	M.P
Untreated catalyst (Control/neat)	Without catalyst	Benzaldehyde	11	49
		Salicylaldehyde	15	50
		Dimethylamino benzaldehyde	16	40.6
H_2SO_4 clay	0.1M	Benzaldehyde	54	50.5
	1M	Benzaldehyde	68	47
	2M	Benzaldehyde	91	49
	3M	Benzaldehyde	86	49.4
Optimized 2M H_2SO_4 clay	2M	Benzaldehyde	91	48.5
		Salicylaldehyde	94	48
		Dimethylamino benzaldehyde	95	48.5

Conclusion

The microwave treatment of Bentonite clay with H_2SO_4 brings about the changes in clay by ion exchange in between the layer of Bentonite clay leads to increasing acidity. The prepared acid activated clay catalyst used as an efficient acid mediated catalyst, easy separation from the reaction products and thus appearing the most suitable catalysts for synthesis of organic compounds with high product yield. The present investigation revealed that small quantity of catalyst required for the synthesis of Schiff bases under solvent free condition using microwave irradiation. The microwave irradiation has highly efficient process for quick organic synthesis with solvent free condition compared with conventional method. The structural analyses of synthesized Schiff bases were confirmed by the study of physical method (M.P), IR and HNMR spectra.

Acknowledgements

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