Journal of Molecular Catalysis A: Chemical 376 (2013) 34–39

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Clay supported titanium catalyst for the solvent free synthesis of tetrasubstituted imidazoles and benzimidazoles

V. Kannan[a], K. Sreekumar[b,*]

[a] Department of Chemistry, Government College Kattappana, Idukki District, Kerala 685 508, India
[b] Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 22, Kerala, India

ARTICLE INFO

Article history:
Received 2 February 2013
Received in revised form 4 April 2013
Accepted 5 April 2013
Available online xxx

Keywords:
Clay
Solvent free synthesis
Imidazoles
Benzimidazoles

ABSTRACT

A series of clay supported metal containing catalysts were prepared and their catalytic performance was evaluated in the synthesis of tetrasubstitued imidazoles under solvent free condition. It was found that K10 supported titanium catalyst showed higher activity compared to other catalysts. The catalysts were characterized by FTIR, XRD, TG/DTA, BET surface area and SEM. The general applicability of the method was demonstrated for the synthesis of tetra- substituted imidazoles from aldehydes and amines containing various electron donating and electron withdrawing substituents. The diversity of the catalyst was studied by synthesis of benzimidazoles and quinoxalines. The mechanism of formation of the products is explained in detail. The catalyst was found to be active for three cycles.

1. Introduction

Imidazoles are important class of compounds in pharmaceutical industries [1]. The imidazole pharmacophore is of therapeutic interest due to its hydrogen bond donor–acceptor capability [2]. Triaryl imidazoles are used as photosensitive material in photography [3]. In addition, they are of interest because of their herbicidal [4], analgesic [5], fungicidal [6], anti-inflammatory [7], anti-allergic activities [8]. They act as ligands in metallo enzymes and non natural metal complexes [9]. They are components of a number of highly significant biomolecules [10]. The imidazole moiety as a part of the side chain in histidine plays a major role in the biological functions of proteins and peptides. Imidazoles can be synthesized using $InCl_3 \cdot 3H_2O$ as catalyst [11], hetero-Cope rearrangement with aldehyde, ammonium acetate and benzil [12], four component condensations of aryl glyoxals, primary amines, carboxylic acids and isocyanides on Wang resin [13] etc. Synthesis of highly substituted imidazole rings cannot be carried out under neutral conditions [14]. Use of conventional acids imposes many disadvantages such as handling, corrosion etc. In the classical approach, for the synthesis of tetrasubstituted imidazoles, cyclo condensations proceeded with low yields after many hours in refluxing AcOH [15]. Keggin type heteropoly acids as solid acid catalysts were recently reported for the synthesis of tetrasubstituted imidazoles [16]. Rafiee et al. reported the synthesis of tetrasubstituted imidazoles under solvent free conditions using various heteropoly acid catalysts [17]. In recent years, considerable interest has been devoted to find a new methodology for the synthesis of highly substituted imidazoles under solvent-free conditions [18,19]. The toxicity and volatile nature of many organic solvents, particularly, chlorinated hydrocarbons that are widely used in large amounts for organic reactions have posed a serious threat to the environment [20,21]. Design of solvent free condition and use of water as solvent are the active area of research in green chemistry [22,23]. Substituted imidazoles are also synthesized by using ionic liquids [24,25]. N-heterocyclic carbenes are generated from substituted imidazoles [26–30].

However search for new reusable catalysts, which are environmentally friendly, is still continuing. Clays are suitable candidates for this purpose. Due to the presence of layered structure, clays are capable of accommodating ligands [31], the metal ions present in the clays can be exchanged with transition metal ions [32]. Clays can be modified with transition metal ions which show Lewis acidity in the range of H_2SO_4 and HNO_3 and satisfies the above mentioned conditions. Here, we report K10 supported titanium as a potential catalyst for the synthesis of tetrasubstituted imidazoles under solvent free conditions.

2. Experimental

2.1. Materials and catalysts

The commercially available clay montmorillonite K10 was obtained from Sigma–Aldrich, Bangalore, India. Benzil, amines, ammonium acetate and solvents were purchased from Merk. Ltd.,

---

* Corresponding author. Tel.: +91 484 2862430/2575804; fax: +91 484 2577595.
E-mail address: ksk@cusat.ac.in (K. Sreekumar).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.04.004

India. Surface area and porosity of clay catalysts were measured by nitrogen adsorption on a Micromeritics Tristar 3100 instrument. TGA and DTA were carried out using simultaneous TG-DTA thermal analyzer of Perkin Elmer Diamond model pyris 6 under a flow of dry Nitrogen. The temperature was raised from room temperature to 1000 °C using a linear program at a heating rate of 10 °C/min. UV–vis DRS spectra were obtained with Varian, Cary 5000 spectrometer. FT-IR spectra were recorded with KBr pellets using a Jasco 4100 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 and 300 MHz NMR spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. Powder X-ray diffraction (XRD) measurements were performed using a Bruker AXS Company, D8 ADVANCE diffractometer. Scans were taken with a 2θ with an increment of 0.05° ranging from 10° to 80° using Cu Kα radiation source generated at 40 kV and 30 mA. The morphology of supported catalyst was studied by scanning electron microscopy (SEM) on a JEOL Model JSM – 6390LV instrument. These analysis were performed at SAIF, STIC, CUSAT.

2.2. Preparation of the catalysts

The clay sample was activated overnight at 100 °C. 3 g of activated clay suspended in 50 ml chloroform was stirred at room temperature under N_2 atm for about 30 min. 2 ml of triethyl amine was added to activate the surface silanol groups and the slurry was stirred for 30 min. Different weight percentage from 1% to 5% (w/w) Titanocene dichloride dissolved in $CHCl_3$ was added under stirring. The slurry was stirred until the color of the suspension was changed from red to yellow over a period of 3 h. This was washed with $CHCl_3$ (30 ml × 3 times). After washing, the solids recovered were calcined under dry oxygen at 500 °C for 8 h. The catalyst is abbreviated as K10Ti.

Sodium exchanged clay was prepared by weighing 1.5 g activated clay, stirred with 0.5 M $NaNO_3$ overnight, washed with water until the filtrate was free from nitrate ions and dried in an air oven at 200 °C. The Co and Cu exchanged clays were prepared by stirring 3 g each of sodium exchanged clay with 25 ml of 0.5 M solution of cobalt(III)chloride and Cu(II)chloride for 24 h, filtered and washed with water until the filtrate was free from chloride ions. The catalyst was dried at 200 °C for 2 h. The catalysts were abbreviated as K10Co, K10Cu and KSFCo, KSFCu respectively.

2.3. Typical procedure for the synthesis of tetrasubstituted imidazoles

A mixture of benzil (2 mmol), benzaldehyde (2 mmol), aniline (2 mmol), ammonium acetate (2 mmol) and 0.250 gm of catalyst was stirred at 120 °C for 2 h, the progress of the reaction was monitored using TLC (Thin Layer Chromatography) using hexane and ethyl acetate (9:1) as elutents. After the completion of the reaction, the crude product was extracted with ethyl acetate followed by filtration. The crude products were further purified by Column Chromatorgraphy using (hexane: ethyl acetate in the ratio 9:1). The products were identified by comparing the results of FT-IR, NMR with those of the authentic samples [33–35].

2.4. General procedure for the synthesis of substituted benzimidazoles/quinoxalines

A mixture of aldehyde/diketone (5 mmol), o-phenylene diamine (5 mmol), and activated K10Ti clay catalyst (0.25 g) was stirred at 120 °C for 2 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was washed with water, extracted with dichloromethane (20 ml), filtered and dried with anhydrous sodium sulphate. The crude products were recrystallised with ethyl acetate.

Table 1
Textural properties of catalysts.

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)
K10Ti	185.26	0.30
KSF Ti	26.79	0.059
K10Cu	233.23	0.41
K10Na	182.21	–
K10	200	0.36
KSF	15	0.11
KSFCo	72.24	0.0084

3. Results and discussion

Different metal supported catalysts were prepared and charactersied. The textural properties of the different catalysts are presented in Table 1.

The prepared catalysts were screened for the synthesis of tetrasubstituted imidazole by selecting, benzil (2 mmol), aldehyde (2 mmol), amine (2 mmol), ammonium acetate (2 mmol) and 500 mg of the catalyst. The reaction mixture was stirred at 100 °C for 2 h; the crude products were separated by extraction using ethyl acetate followed by filtration. The K10Ti was selected as the catalyst of choice because, it gave best results. The results are summarized in Table 2.

3.1. Catalyst characterization

The UV-DRS spectra of the parent and modified catalyst showed a band around 220 nm, 260–270 nm. Spectra of Ti/Si catalysts are characterized by broad absorption band centered around 220 nm, ~260–270 nm and above 330 nm, as reported by Zhang et al. [36]. Band at ~220 nm in Ti/Clay catalyst is associated with isolated Ti (IV) sites, shoulder at 270 nm is probably due to partially polymerized hexacoordinate Ti species.

The SEM image of the catalyst shows that the crystalline nature of the clays was maintained and the Ti metal is uniformly distributed (Fig. 1). The SEM result is supported by XRD results. XRD pattern of the catalyst (Fig. 2) indicates that the basic clay structure is maintained after modification. The FT-IR spectra of montmorillonite K10 and titanium incorporated montmorillonite K10 are shown in Fig. 3. The band around 1010 cm^{-1} was broadened indicating the successful incorporation of titanium in the clay. The band at 950 cm^{-1} (Si—O—Ti) was merged with band at 1010 cm^{-1}. Thermal stability of the catalyst was studied by TG/DTA analysis under nitrogen flow. The weight loss in the region 80–150 °C may be attributed to the loss of adsorbed water in the catalyst system. The weight loss between 200 °C and 300 °C may be due to the loss of hydrated water (Fig. 4).

The decrease in the surface area and pore volume obtained from BET results (from 200 m^2/g to 185.2 m^2/g and 0.36 cm^3/g to 0.3 cm^3/g for the K10Ti sample is ascribed to the incorporation

Table 2
Synthesis of tetrasubstituted imidazoles using metal supported catalysts.

Samples	Time (h)	Yield (%)[a]
K10Ti	2	80
KSFTi	2	46
K10Cu	2	61
K10	2	62
KSF	2	30
KSFCo	2	34

Mole ratio. Aniline:benzaldehyde:benzil: ammonium acetate is 1:1:1:1.2.
[a] Yields refer to isolated crude products.

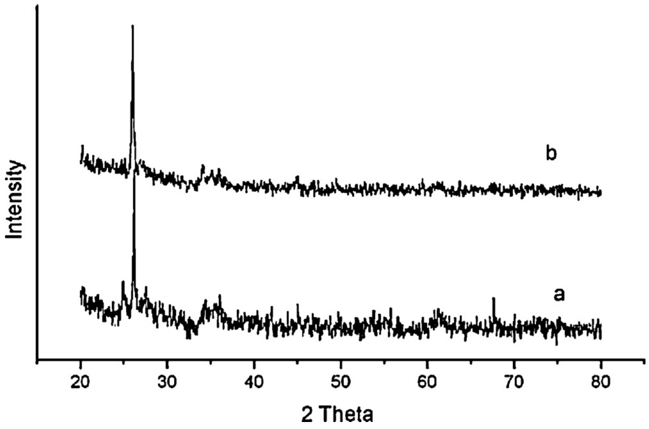


Fig. 1. SEM image of K10Ti.

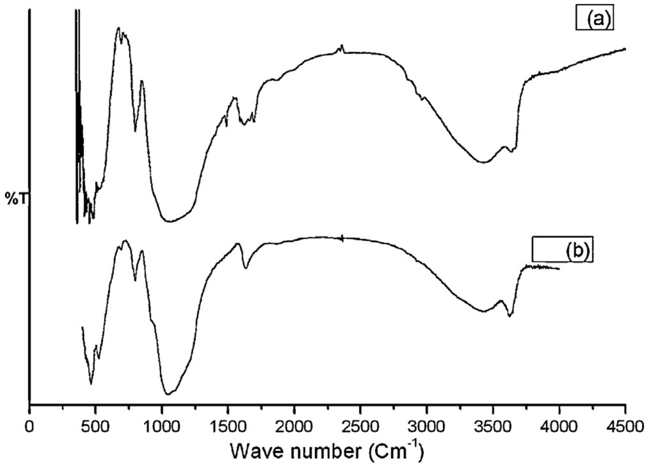


Fig. 2. XRD pattern (a) K10 and (b) K10Ti.

of titanium in the clay framework. This is also supported by the relatively low initial adsorption isotherm plot (Fig. 5).

3.2. Pyridine adsorption studies of the catalyst

Adsorption of pyridine on the surface of catalysts is one of the most frequently used methods for the determination of surface acidity. The use of IR spectroscopy to detect adsorbed pyridine enables us to distinguish different acid sites. The presence of acidity (Bronsted and Lewis acidity) was determined for K10Ti using pyridine adsorption with FT-IR Spectroscopy (Fig. 6). The catalyst showed Bronsted and Lewis acidity at 1492 cm^{-1} and 1450 cm^{-1}, respectively which was assigned to pyridine molecules interacting

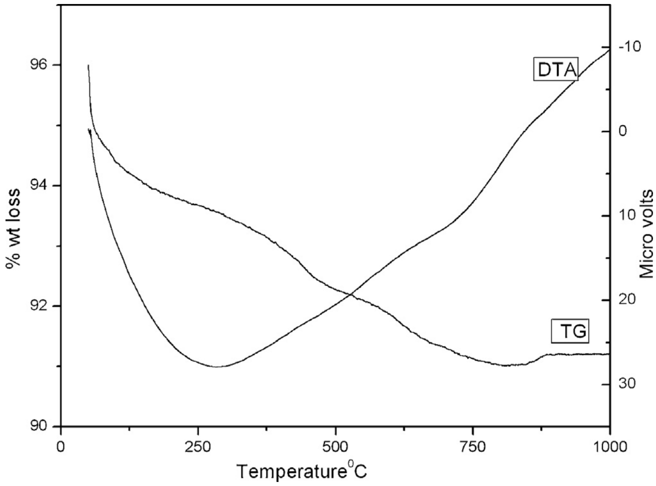


Fig. 3. IR Spectra of (a) K10Ti and (b) K10.

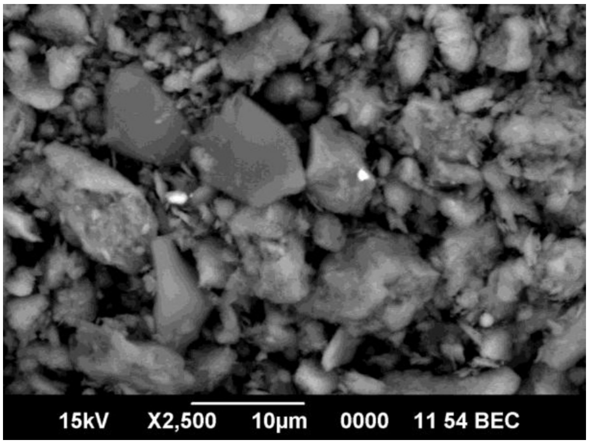


Fig. 4. TG/DTA of K10Ti.

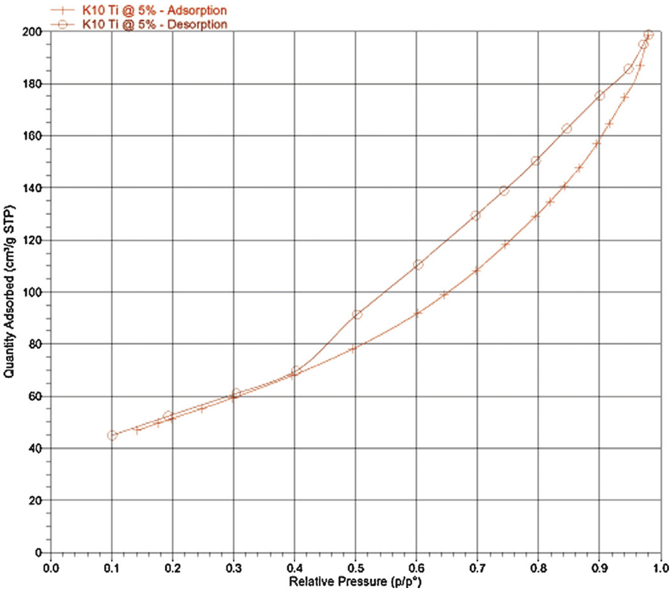


Fig. 5. Adsorption isotherm of K10Ti.

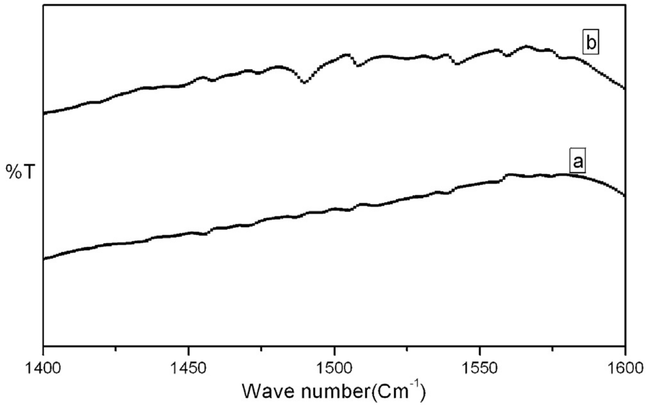
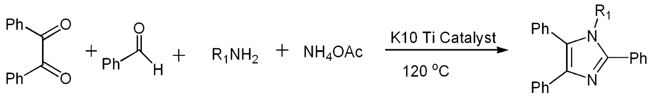


Fig. 6. FT-IR spectra of pyridine adsorbed (a) K10 and (b) K10Ti.



Scheme 1. Synthesis of tetrasubstituted imidazoles.

with Bronsted and Lewis acid sites of the catalyst. It is shown in earlier reports that Bronsted acid sites in the vicinity of Lewis acidic metal center (active sites) act as co catalyst [37,38]. The mechanism can be written as Bronsted acid catalyzed or Lewis acid catalyzed reaction.

3.3. *Catalytic activity studies*

Several methods are used for the synthesis of tetrasubstituted imidazoles and their derivatives. Tetrasubstituted imidazoles are generally synthesized in a four component condensation of aldehydes, 1,2-diketones, amines and ammonium acetate in acetic acid or on various supports such as acidic, basic, and neutral alumina, bentonite, montmorillonite K10, KSF and Silica gel. The reported methods suffer from low yield and longer reaction time or using rigorous acid treatment. Among the reported methods, those using clays deserve mention as a convenient laboratory method for the synthesis of these compounds. To the best of our knowledge, no reports have been found in the use of clay supported titanium catalyst using titanocene dichloride as the titanium source for the synthesis of tetrasubstituted imidazoles. The catalyst was also found good for the synthesis of benzimidazoles. This method not only affords the product in excellent yields, but also avoids the problems associated with handling, safety and pollution. This catalyst can act as eco-friendly for a variety of organic transformations. It is non- volatile, recyclable, non-explosive and easy to handle.

Tetrasubstitued imidazoles were synthesized using clay supported titanium catalyst under solvent free condition invoking 1 mmol aldehyde, 1 mmol benzil, 1 mmol amine, 1.2 mmol NH_4OAc under solvent free condition in a sealed glass apparatus (Scheme 1). The catalyst loading was varied as 0.05 g, 0.1 g, 0.15 g 0.2 g, 0.25 g and 0.3 g. With increase in catalyst loading, the yield was found to increase up to 0.25 g further increase has no effect on the yield. The optimum catalyst loading was taken as 0.25 g. Similarly, temperature of the reaction was varied from 80 °C to 120 °C, the yield was found to increase with increase in temperature up to 120 °C, and further increase resulted in the formation of a charred product. The optimum temperature for the reaction was selected as 120 °C. Different aldehydes and amines were studied at optimized reaction conditions, all the substrates gave good yield irrespective of the electron donating or withdrawing groups attached on them. The results are summarized in Table 3. The mechanism of formation of tetrasubstiuted imidazoles mediated by the clay supported titanium catalyst is given in Scheme 2

The products were characterized by ^1H NMR, IR and through comparison of the physical properties with those reported in the literature.

3.3.1. *Characterization of selected products*

(Entry 1, Table 3), Mp: 220 °C; IR υ_{max} (cm^{-1}): 2986 (C—H), 1600 (C=C), 1580 (C=N), ^1H NMR, (300 MHz, $CDCl_3$); δ (ppm); δ 6.80–7.60 (m, 20H).

(Entry 2, Table 3), Mp: 105 °C; IR υ_{max} (cm^{-1}): 2982 (C—H), 1589 (C=C), 1574 (C=N), ^1H NMR, (300 MHz, $CDCl_3$); δ (ppm); δ 6.4–8.2 (m, 15H) 7.4–7.6 (dd, 4H J = 7 Hz).

(Entry 3, Table 3), Mp: 255 °C; IR υ_{max} (cm^{-1}): 2987 (C—H), 1604 (C=C), 1510 (C=N), ^1H NMR, (300 MHz, $CDCl_3$); δ (ppm); δ 7–7.45 (m, 15H, Ph) 7.58 (d, 1H, J = 8.3 Hz) 7.8 (d, 1H, J = 7.8 Hz), 8–8.1 (d, 1H, J = 8.1 Hz) 8.24 (s, 1H).

Table 3
Solvent free synthesis of tetrasubstituted imidazoles using K10Ti.

Sl. no.	R^1	R^2	Time (h)	Yield % [a]
1	C_6H_5	C_6H_5	2.5	78
2	4-ClC_6H_4	C_6H_5	2	80
3	3-$NO_2C_6H_4$	C_6H_5	2	81
4	C_6H_5	$C_6H_5CH_2$	3	84
5	C_6H_5	CH_3	4	68
6	4-$NO_2C_6H_5$	CH_3	2.5	76
7	C_6H_5	4-BrC_6H_4	3.5	74
8	Thiophene	C_6H_5	3	69
9	C_6H_5	C_2H_5	4	72
10	3-NO_2 C_6H_4	C_2H_5	2.5	74
11	4-Cl C_6H_5	C_2H_5	3	73
12	Thiophene	CH_3	3	72
13	4-Br C_6H_4	C_6H_5	3.5	78
14	4-Cl C_6H_4	$C_6H_5CH_2$	4	79
15	Thiophene	$C_6H_5CH_2$	3	71

Aldehyde (1 mmol): amine (1 mmol), benzil (1 mmol), NH_4OAc (1.2 mmol), catalyst: K10Ti (0.25 g).
[a] Yields refer to isolated pure products.

(Entry 4, Table 3), Mp: 167 °C; IR υ_{max} (cm^{-1}): 2982 (C—H), 1600(C=C), 1574 (C=N), ^1H NMR, (400 MHz, $CDCl_3$); δ (ppm); 5 (2H, s, CH_2), 6.9–7.7 (20H, m, Ar—H).

(Entry 5, Table 3), Mp: 142 °C; IR υ_{max} (cm^{-1}): 2889 (C—H), 1602 (C=C), 1531 (C=N), ^1H NMR, (300 MHz, $CDCl_3$); δ (ppm); δ 7.2–7.7 (m, 15H), 3.5 (s, 3H).

(Entry 6, Table 3), Mp: 172 °C; IR υ_{max} (cm^{-1}): 2982 (C—H), 1592 (C=C), 1530 (C=N), ^1H NMR, (400 MHz, $CDCl_3$);δ (ppm); 7.1–8.5 (14H, m Ar—H), 3.3 (3H, s).

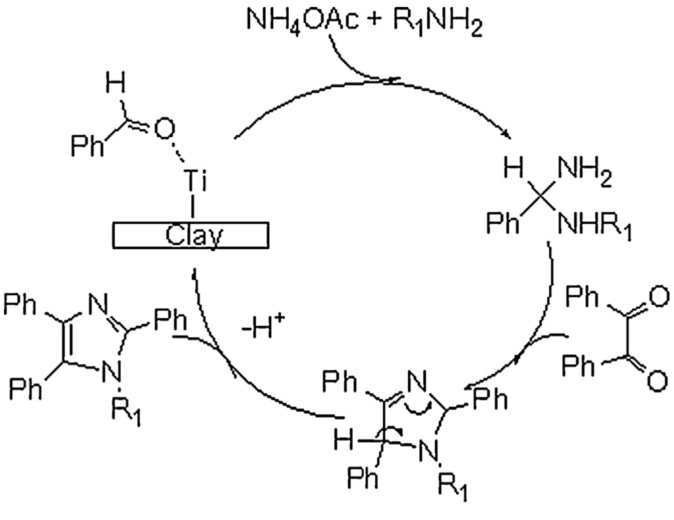
(Entry 7, Table 3), Mp: 168 °C; IR υ_{max} (cm^{-1}): 2986 (C—H), 1592 (C=C), 1477 (C=N), ^1H NMR, (400 MHz, $CDCl_3$); δ (ppm); 5.1 (2H, s, CH_2), 6.9–7.7 (20H, m, Ar—H).

(Entry 8, Table 3), Mp: 162 °C; IR υ_{max} (cm^{-1}): 2986 (C—H), 1600 (C=C), 1574 (C=N), ^1H NMR, (300 MHz, $CDCl_3$); δ (ppm); 6.5–7.6 (18H, m, Ar—H).

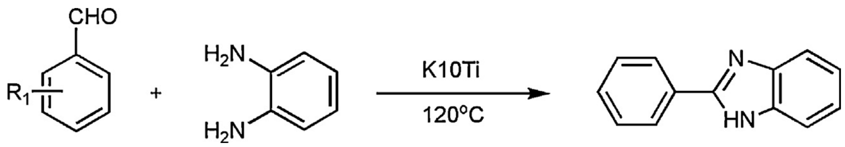
(Entry 9, Table 3), Mp: 169 °C; IR υ_{max} (cm^{-1}): 2985 (C—H), 1600 (C=C), 1574 (C=N), ^1H NMR, (400 MHz, $CDCl_3$); δ (ppm); 7–7.8 (15H, m, Ar—H), 4.1 (2H, q, J = 6.969 Hz) 1.1 (3H, t, J = 7.18 Hz).

(Entry 10, Table 3), Mp: 166 °C; IR υ_{max} (cm^{-1}): 2982 (C—H), 1605 (C=C), 1510 (C=N), ^1H NMR, (400 MHz, $CDCl_3$); δ (ppm); 7.1–8.7 (m, 19H, Ar—H), 4.1 (q, 2H, J = 7.143 Hz) 1.1 (3H, t, J = 7.026 Hz).

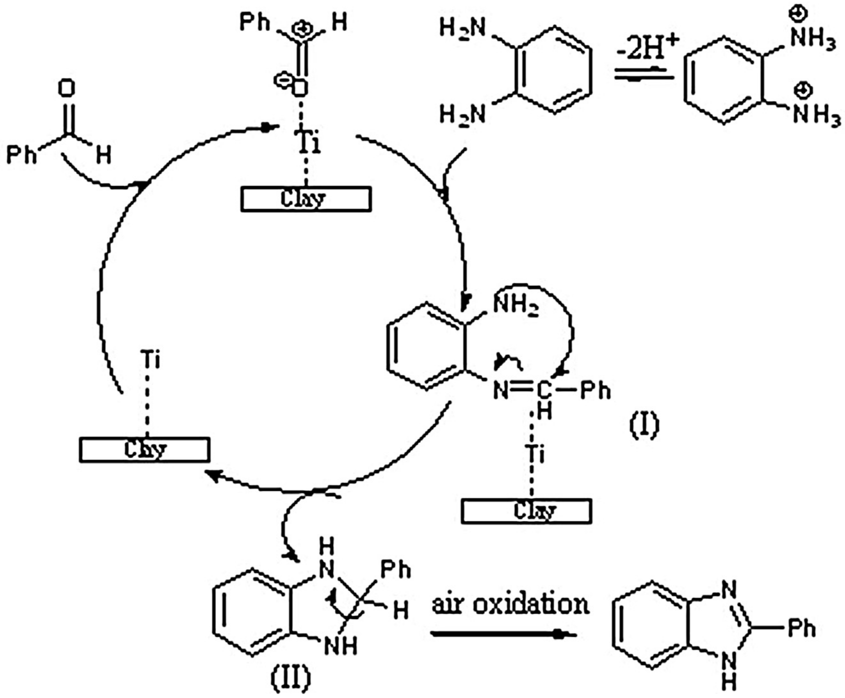
(Entry 1, Table 4), Mp: 294 °C ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8–8.2 (m, 2H), 7.6 (dd, 2H, J = 8, 3.2 Hz), 7.2–7.6 (m, 5H), 4.9 (s, 1H).



Scheme 2. Plausible mechanism of formation of tetrasubstituted imidazoles on clay supported Ti catalyst.



Scheme 3. Synthesis of benzimidazoles using K10Ti as catalyst.



Scheme 4. Proposed mechanism of titanium catalyst assisted benzimidazole synthesis.

(Entry 2, Table 4), Mp: 294 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.0 (d, 2H, J = 8.2 Hz), 7.6 (m, 2H, J = 8.2 Hz), 7.2 (d, 2H, J = 7.6 Hz), 70.7.2 (m, 2H) 4.8 (s, 1H), 2.4 (s, 3H).

(Entry 3, Table 4), Mp: 224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.4 (d, 2H, J = 7.4 Hz), 7–7.2 (m, 4H), 6.6 (d, 2H, J = 7.8) 4.6 (s, 1H), 3.7 (s, 3H).

(Entry 4, Table 4), Mp: 289 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.2 (d, 2H, J = 8.4 Hz), 7.4 (d, 2H, J = 8.4 Hz) 7–7.2 (m, 2H), 6.6 (d, 2H, J = 7.8) 4.6 (s, 1H).

(Entry 5, Table 4), Mp: 314 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.0–8.2 (m, 2H), 7.1–7.2 (m, 2H), 6.7–6.9 (m, 4H), 4.4 (s, 1H).

The mechanism involves the participation of titanium Lewis acid sites. The catalyst may contain a mixture of $(SiO)_2TiCl_2$, $SiOTiCl_3$ and $(SiO)_3TiCl$, titanium sites. The mechanism is explained by considering the participation of Ti species of the clay matrics.

Table 4
Synthesis of benzimidazoles and quinoxaline derivatives.

Entry	R	Product	Yield% [a]
1	H	2a	79
2	CH_3	2b	74
3	OCH_3	2c	62
4	4-Cl	2d	82
5	4-NO_2	2e	71
6	Thio	2f	68
7	Benzil[b]	2g	91

Mole ratio. Aldehyde, o-phenylene diamine, 1:1, K10Ti catalyst (0.25 g), Temparature 120 °C, reaction time, 2 h.

[a] Yields refer to isolated pure products.

[b] Quinoxaline.

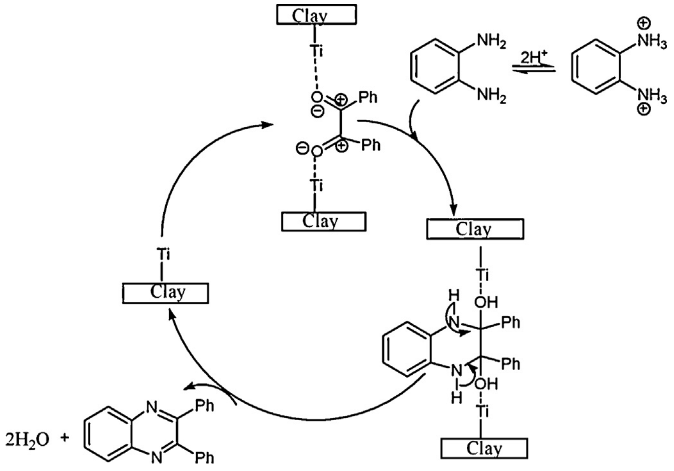
The general applicability of the catalyst was verified by the synthesis of benzimidazoles and quinoxalines. The synthesis of benzimidazoles was carried out by the reaction of aldehyde and orthophenylene diamine under solvent free condition. The synthesis of substituted benzimidazoles using conventional heating was carried out for a series of aldehydes using the clay supported titanium catalyst (Scheme 3). The results are summarized in Table 4.

The reaction between an aldehyde and a diamine leads to the formation of Schiff base (I) which is stabilized by clay supported titanium catalyst. Intramolecular attack by the second amino group on C=N double bond facilities the formation of hydrobenzimidazole (II) which undergoes subsequent air oxidation to give the desired benzimidazole as the final product (Scheme 4).

Clay supported titanium catalyst facilitates the formation of quinoxaline derivatives as outlined in the mechanism (Scheme 5). 1,2-Diketone was stabilized in the interlayer of clay via interaction with Ti^{4+} by partial polarization of carbonyl group which reacts readily with o-phenylenediamine. The resultant amino-1,2-diol undergoes dehydration to give quinoxaline as the end product.

3.4. Recyclability

Finally, the catalyst recyclability was considered, and the catalyst was found to be stable over three cycles without appreciable loss in activity.



Scheme 5. Proposed mechanism of titanium catalyst assisted quinoxaline synthesis.

4. Conclusion

The clay supported titanium catalyst was found to be an effective catalyst for the synthesis of tetrasubstituted imidazoles. The diversity of the catalyst was studied by the synthesis of benzimidazoles and quinoxaline. The mechanism of formation was explained in these cases. The catalytic activity may be correlated with the Lewis acid and Bronsted acid sites together as supported by pyridine adsorbed IR spectral studies. SEM and XRD results showed that the dispersion of titanium was uniform in the clay framework and basic structure of the clay was maintained. The method reported here is simple; the catalyst can be easily separated after the reaction and can be reused. The proposed catalyst is thermally stable and can be applied for the synthesis of a series of similar organic compounds.

Acknowledgments

One of the authors KV is grateful to UGC for teacher fellowship. Help received from SAIF CUSAT, NMR Research Centre IISc, Bangalore are greatly acknowledged for the NMR spectra, XRD and SEM analysis.

References

[1] B.L. Vallee, D.S. Auld, Biochemistry 29 (1990) 5647–5659.
[2] S.K. Thompson, K.H.M. Murthy, B. Zhao, E. Winborne, D.W. Green, S.M. Fisher, R.L. Desjarlais, T.A. Tomaszek, T.D. Meek, J.G. Gleason, S.S. Abdelmeguid, J. Med. Chem. 37 (1994) 3100–3107.
[3] H. Sensui, J. Ichikawa, S. Sato, Jpn. Kokai Tokyo Koho, JP 62,94,841;
H. Sensui, J. Ichikawa, S. Sato, Chem. Abstr. 107 (1987) 187436q.
[4] T. Maier, R. Schmierer, K. Bauer, H. Bieringer, H. Buerstell, B. Sachse, US Patent, 820 335A (1989);
T. Maier, R. Schmierer, K. Bauer, H. Bieringer, H. Buerstell, B. Sachse, Chem. Abstr. 111 (1989) 19494.
[5] S.E. Wolkenberg, D.D. Wisnosak, W.H. Leister, Y. Wang, Z. Zhao, C.W. Lindsley, Org. Lett. 6 (9) (2004) 1453–1456.
[6] A.F. Pozherskii, A.T. Soldatenkov, A.R. Katritzky, Heterocycles in Life Society, Wiley, New York, 1997179.
[7] J.G. Lombardino, E.H. Wiseman, J. Med. Chem. 17 (1974) 1182–1188.
[8] J.W. Blank, G.J. Durant, J.C. Emmett, C.R. Ganellin, Nature 248 (1974) 65–67.
[9] B.A. Omotowa, J.M. Shreeve, Organometallics 23 (2004) 783–791.
[10] P. Koch, C. Bäuerlein, H. Jank, S. Laufer, J. Med. Chem. 51 (2008) 5630–5640.
[11] S.D. Sharma, P.H. Hazarika, D. Konwar, Tetrahedron Lett. 49 (2008) 2216–2220.
[12] I. Lantos, W.Y. Zhang, X. Shui, D.S. Eggleston, J. Org. Chem. 58 (1993) 7092–7095.
[13] S. Sarshar, D. Sive, A.M.M. Mjalli, Tetrahedron Lett. 37 (1996) 835–838.
[14] E.L. Beccalli, A. Majori, C. Marchesini, Torricelli, Chem. Lett. 9 (1980) 659–662.
[15] E.J. Zhang, T.F. Moran, Woiwode, A.M.M. Mjalli, Tetrahedron Lett. 37 (1996) 751–754.
[16] M.M. Heravi, F. Derikvand, F. Bamoharram, J. Mol. Catal. A: Chem. 263 (2007) 112–114.
[17] E. Rafiee, H. Mahdavi, M. Joshaghani, Mol. Divers. 151 (2011) 125–134.
[18] D.E. Frantz, L. Morency, A. Soheili, J.A. Murry, E.J. Grabowski, R.D. Tillyer, Org. Lett. 6 (2004) 843–846.
[19] J. Sisko, M.Mellinger, Pure Appl. Chem. 74 (2002) 1349–1358.
[20] W.M. Nelson, Green Chemistry, Oxford University Press, Oxford, 1998.
[21] J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, Synthesis (2003) 2661–2666.
[22] K. Tanaka, F. Toda, Chem. Rev. 100 (2000) 1025–1074.
[23] G.W.V. Cave, C.L. Raston, J.L. Scott, Chem. Commun. 21 (2001) 2159–2169.
[24] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley VCH, Weinheim, 2003.
[25] T. Welton, Chem. Rev. 99 (1999) 2071–2084.
[26] H.L. Lee, M. Bang, C.S. Pak, Tetrahedron Lett. 46 (2005) 7139–7142.
[27] J.M.D. Storey, C. Williamson, Tetrahedron Lett. 46 (2005) 7337–7339.
[28] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290–1309.
[29] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39–92.
[30] W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162–2187.
[31] V.C. Rode, V.S. Kshirsagar, J.M. Nadgeri, K.R. Patil, Ind. Eng. Chem. Res. 46 (2007) 8413–8419.
[32] W.Trakarnpruk, Dumrongpong, J. Mater. Sci. 41 (2006) 3001–3006.
[33] A.R. Karimi, A. Alimohoammadi, J. Azizian, A.A. Mohammadi, M.R. Mohammadizadeh, Catal. Commun. 7 (2006) 728–732.
[34] S. Balalaie, A. Arabanian, Green Chem. 2 (2000) 274–276.
[35] S. Kantevari, S.V.N. Vuppalapati, D.O. Biradar, L. Nagarapu, J. Mol. Catal. A: Chem. 266 (2007) 109–113.
[36] W. Zhang, J. Wang, P.T. Tanev, T.J. Pinnavaia, J. Chem. Soc. Chem. Commun. (1996) 976–980.
[37] J. Penzien, T.E. Muller, J.A. Lercher, Chem. Commun. 18 (2000) 1753–1754.
[38] J. Penzien, R.Q. Su, T.E. Muller, J. Mol. Catal. A: Chem. 182 (2002) 489–498.