



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

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## ABSTRACT

A series of clay supported metal containing catalysts were prepared and their catalytic performance was evaluated in the synthesis of tetrasubstituted 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.

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## 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  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  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  $\text{AcOH}$  [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  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  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.,

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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. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 and 300 MHz NMR spectrometer with CDCl<sub>3</sub> 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<sub>2</sub> 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<sub>3</sub> 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<sub>3</sub> (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<sub>3</sub> 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 eluents. 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 Chromatography 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),

**Table 1**  
Textural properties of catalysts.

Samples	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
K10Ti	185.26	0.30
KSFTi	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

filtered and dried with anhydrous sodium sulphate. The crude products were recrystallised with ethyl acetate.

## 3. Results and discussion

Different metal supported catalysts were prepared and characterized. 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<sup>-1</sup> was broadened indicating the successful incorporation of titanium in the clay. The band at 950 cm<sup>-1</sup> (Si–O–Ti) was merged with band at 1010 cm<sup>-1</sup>. 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<sup>2</sup>/g to 185.2 m<sup>2</sup>/g and 0.36 cm<sup>3</sup>/g to 0.3 cm<sup>3</sup>/g for the K10Ti sample is ascribed to the incorporation

**Table 2**  
Synthesis of tetrasubstituted imidazoles using metal supported catalysts.

Samples	Time (h)	Yield (%) <sup>a</sup>
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.

<sup>a</sup> Yields refer to isolated crude products.

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