



# Modified Montmorillonite clay catalyzed regioselective ring opening of epoxide with amines and alcohols under solvent free conditions

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## ABSTRACT

Modification of Montmorillonite by acid treatment depletes the layered structure and generates micro- and mesopores. The catalytic activity of naturally occurring Montmorillonite clay modified by acid treatment is reported for the reactions of epoxides with nucleophiles such as amines and alcohols at ambient temperature and solvent-free condition. The solid acid catalyst of the present study is reusable and exhibits significantly higher catalytic activities than known catalysts for the opening of the oxirane ring with nitrogen (aromatic as well as aliphatic amines) and oxygen (aromatic as well as aliphatic alcohols). A wide range of  $\beta$ -amino alcohols and  $\beta$ -alkoxy alcohols are synthesized with high epoxide conversion of excellent regioselectivity. The modified catalyst is recycled up to five times without significant loss in conversion and selectivity.

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## 1. Introduction

Epoxides are small molecules with wide range of synthetic applications as intermediates in pharmaceutical and agrochemical industries. The three-membered heterocyclic epoxide ring offers an uncommon combination of reactivity, synthetic flexibility, and atom economy. It is susceptible to attack by a range of nucleophiles, including nitrogen (e.g., ammonia, amines, azides), oxygen (e.g., alcohols, phenols), and sulfur containing compounds, leading to bifunctional molecules of great industrial value.  $\beta$ -Amino alcohol moiety is a main structural unit in a vast number of naturally occurring and synthetic molecules of pharmaceutical importance. Ring opening of epoxides with amines and alcohols yields  $\beta$ -amino alcohols and  $\beta$ -alkoxy alcohols which are the key intermediates in the synthesis of a vast range of biologically active natural and synthetic products [1], unnatural amino acids [2], and chiral auxiliaries for asymmetric synthesis [3]. The nucleophilic ring opening of epoxides with amines constitutes a well recognized route for the synthesis of  $\beta$ -amino alcohols [4]. The classical synthetic approach for the synthesis involving heating of epoxides with large excess of

amines at elevated temperature [5], works less well with poorly nucleophilic amines. Moreover, the lack of appreciable regioselectivity, the requirements for high temperature (which poses problems in dealing with sensitive epoxides), and the need for an excess of amine in the classical methods of  $\beta$ -amino alcohol synthesis have led to the necessity for activation of the epoxides so as to increase their susceptibility to nucleophilic attack by amines. The various methodologies developed for this reaction include the use of sulfamic acid [6], amberlyst resin [7], alumina [8], metal amides [9], metal alkoxides [10], metal triflates [11], transition metal halides [12], alkali metal perchlorates, [13] rare earth metal halides, [14] silica under high pressure, [15] ionic liquids [16], zeolites [17], Montmorillonite K-10 [18], and Lewis acids in a supercritical carbon dioxide [19]. However, these methodologies suffer from one or more disadvantages such as long reaction times, elevated temperatures, moderate yields, use of air or moisture sensitive catalysts, requirement of stoichiometric amounts of catalyst, costly reagents/catalysts, rearrangement to allylic alcohols [20], potential hazards in handling pyrophoric/moisture sensitive reagents in the preparation of the catalyst, and in most of the cases being applicable to aromatic amines only. The ring opening of epoxides in water in the absence of any catalyst was reported, but involved a long reaction time, and the product yield was also low [21,22]. Even though heterogeneous catalysts have been used in the ring-opening addition of nucleophiles like amines and alcohols to epoxides, their activity and selectivity are found to be low.

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Brønsted acidic SBA-15 functionalized with sulfonic acid, Ti-SBA-12, Ti-SBA-16 and Lewis acidic Ti-MCM-41 catalyze the reaction at mild conditions yielding good conversion and product selectivity [23,24]. Therefore, the development of a better catalyst for the activation of epoxides rendering them more susceptible to nucleophilic attack under milder conditions is in high demand.

Clay catalysts have attracted considerable attention as catalysts for a variety of organic reactions [25,26]. The clays most frequently used in catalysis are the smectites. The acidity of a clay matrix can be improved by cation exchange, acid activation, pillaring, etc. Cation exchanged clays are known to be good Brønsted acid catalysts. The Brønsted acidity is generated due to dissociation of hydrated water molecule coordinated to interlayer cations [25]. Modification by acid treatment breaks the layers of smectite group clays. Acid activated clays are used as catalysts, catalyst beds, adsorbents, and bleaching earth in industry. Acid activated clays constitute a widely available inexpensive solid source of protons, which are effective in a number of important organic reactions and processes. The catalytic activity usually reflects the extent of leaching of the raw clay which, in turn, depends upon the acid-treatment conditions [27–30]. The acid treated clays are also being used as support for generation of metal nanoparticles, which are being employed as efficient catalyst for various organic reactions [31–35].

In the present work, the porous matrix obtained after acid treatment on naturally occurring Montmorillonite clay is used as efficient reusable heterogeneous catalyst for ring opening of epoxides with amines and alcohols to generate  $\beta$ -amino alcohols and  $\beta$ -alkoxy alcohols with high conversion and excellent product selectivity.

## 2. Experimental

### 2.1. Preparation of catalyst

Naturally occurring Montmorillonite clay (procured from Gujarat, India) containing silica sand, iron oxide, etc. as impurities was purified by standard sedimentation method to collect particles less than  $2\ \mu\text{m}$  fraction [36]. The oxide composition of the clay determined by weight chemical and flame photometric methods as reported earlier [37]. The purified clay (1 g) was refluxed with 4 M HCl acid (100 mL) for various time intervals (15 min, 1 h, 2 h and 4 h). The slurry was cooled down to room temperature, filtered and washed thoroughly with water and was dried in an air oven at 393 K for 12 h [37,38]. The clay samples thus prepared are designated as H-Mont.-1, H-Mont.-2, H-Mont.-3 and H-Mont.-4 respectively.

### 2.2. Characterization of the catalyst

The characterizations of the catalysts were carried out similarly as reported [37,38]. The oxide compositions of the clay determined by weight chemical and flame photometric methods were  $\text{SiO}_2$ : 49.42%;  $\text{Al}_2\text{O}_3$ : 20.02%;  $\text{Fe}_2\text{O}_3$ : 7.49%;  $\text{MgO}$ : 2.82%;  $\text{CaO}$ : 0.69%;  $\text{LOI}$ : 17.51%; others ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{TiO}_2$ ) 2.05%. IR spectra ( $4000\text{--}400\ \text{cm}^{-1}$ ) were recorded on KBr pellets in a Shimadzu IR Affinity-1 spectrophotometer. Powder XRD spectra were recorded on a Rigaku Ultima IV from  $2\text{--}80^\circ\ 2\theta$  using a  $\text{CuK}\alpha$  source ( $\lambda = 1.54\ \text{\AA}$ ). Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Specific surface area of the samples was measured by adsorption of nitrogen gas at 77 K and applying the Brunauer–Emmett–Teller (BET) calculation. Prior to adsorption, the samples were degassed at  $250^\circ\text{C}$  for 3 h. Pore size distributions were derived from desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. To measure the acidity,  $\text{NH}_3$ -TPD was carried out in a Quantachrome ChemBET Pulsar machine. The TPD measurement was carried out

from 373 K to 1073 K. The clay sample was preheated at 573 K and then cooled down to 323 K, and then  $\text{NH}_3$  was adsorbed for 30 min. The samples were flushed with He for 1 h at 373 K, and the desorption was monitored by raising the temperature. Scanning Electron Microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) patterns were obtained from Leo 1430 vp operated at 10 kV and 3 kV.  $^1\text{H}$  NMR was recorded at room temperature in a Bruker AC 200 spectrometer using  $\text{CDCl}_3$  as a solvent. Mass spectra were determined in a Bruker Daltonics Esquire 3000 LC-ESI Ion Trap Mass Spectrometer.

### 2.3. Ring opening of epoxide with amine

Ring opening of epoxide with amines was carried out by taking a known quantity of the catalyst (H-Mont), epoxide and equimolar amount of amine in a 10 ml single-necked round-bottom flask. The reaction was conducted at room temperature and for a desired period of time. The progress of the reaction was monitored by taking out aliquots of the sample, diluting it with a known quantity of dichloromethane, separating the catalyst by centrifugation and subjecting the diluted liquid to gas chromatographic analysis (Chemito GC, Model 8510, and FID). In some cases, the products were isolated by column chromatography (eluent: hexane–ethyl acetate mixture).

### 2.4. Ring opening of epoxide with alcohol

Ring opening of epoxide with alcohol was carried out by taking equimolar amounts of epoxide and alcohol and a known quantity of the catalyst in a 10 ml single-necked round-bottom flask at room temperature. The progress of the reaction was monitored as done for aminolysis by subjecting the diluted liquid to gas chromatographic analysis (Chemito GC, Model 8510, FID).

## 3. Results and discussion

The powder XRD patterns of different acid activated Montmorillonite along with parent clay are shown in the Fig. 1. The parent

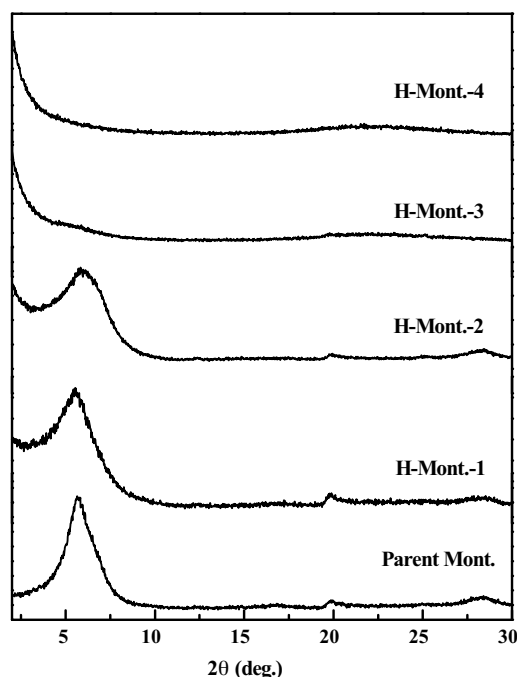


Fig. 1. Powder XRD pattern of parent Montmorillonite and acid treated Montmorillonite clay.

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