

Letter

Iron pillared clay — an efficient catalyst for ring opening of oxiranes¹

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Abstract

Nucleophilic ring opening of oxiranes with aniline, TMSN_3 and TMSCN were catalysed by iron pillared clay (FePILC-K10) in quantitative yields under mild reaction conditions. The catalyst was reused for several cycles with consistent activity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent times, considerable progress has been made in the development of catalytic methodologies involving ring opening of epoxides for cyanohydrin, trimethylsilyl and azidosilyl ethers. These ethers are important intermediates in the synthesis of cyanohydrins, β -amino alcohols, α -amino acids and other biologically active compounds [1,2]. Conventional methods include the various homogeneous Lewis acid

catalysts like ZnI_2 [3], AlCl_3 , LaCl_3 [4], metal tartrates [5], SmCl_3 [6], KCN-18-Crown-6, $\text{Bu}_4\text{N}^+\text{CN}^-$ [7]. Present situation warrants the replacement of toxic, corrosive Lewis acids by ecofriendly solid acids and bases such as zeolites [8], clays [9,10] and hydrotalcites [11,12], etc., for nucleophilic additions and in other Friedel–Crafts reactions. Onaka et al. [10] reported strongly acidic Fe-montmorillonite and non-acidic CaF_2 and hydroxyapatite are efficient solid catalysts for cyanosilylation of carbonyl compounds. Recently, we have reported the ring opening of oxiranes with Mn-salen mesoporous materials [13] and $\text{MgAlCO}_3\text{-HT}$ [12], which required comparatively longer reaction times. Pillared clays [14] are materials of increasing potential interest because of their

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properties as catalysts for alcohol dehydration, alkylation, hydrocarbon cracking and other acid-promoted reactions. Pillared clays are prepared by the intercalation of metal hydroxy-oxy oligomers between the silicate layers of smectite-type clays. Our recent reports point out iron pillared clays (FePILC–K10) are the most efficient catalysts for Friedel–Crafts alkylation [9] and acylation [15] of aromatic hydrocarbons. This prompted us to test the efficacy of FePILC–K10 catalysts for these ring opening reactions.

2. Experimental section

2.1. Preparation of catalysts

K10, an acid-treated montmorillonite that essentially shows mesopores of ~ 3 nm and Kunipia clay were procured from Fluka and Japan, respectively. They were used as such without any further treatment. Iron exchanged catalyst was obtained from mesoporous K10 by ion-exchange method described in Ref. [16]. FePILC–K10 was prepared in accordance with the procedure reported by Rightor et al. [17].

2.2. Typical procedure

In a two-necked round bottom flask, 0.098 g (1 mmol) of cyclohexene oxide, 0.093 g (1 mmol) of aniline and 0.050 g of catalyst in 10 ml of THF were stirred vigorously at 70°C for 1.5 h. The reaction was monitored by thin layer chromatography (TLC). The work-up comprises of simple filtration and evaporation of filtrate under reduced pressure to afford the pure product. Yield: 0.182 g (95%). The product was analysed by NMR, IR and Mass spectra, which were in accordance with those obtained by literature procedures [5]. IR (KBr), ν 3400, 1580,

1500, 1280 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz), δ 1.00–1.52 (m, 4H), 1.55–1.88 (m, 2H), 1.88–2.24 (m, 2H), 2.86–3.45 (m, 2H), 3.34 (s, 2H), 6.48–6.5 (m, 3H), 6.96–7.23 (m, 2H); MS, 191 (M^+).

3. Results and discussion

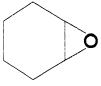
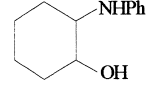
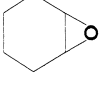
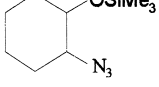
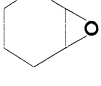
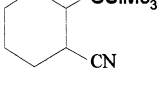
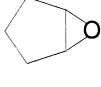
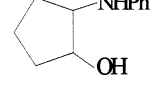
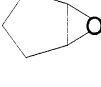
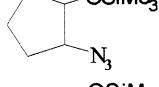
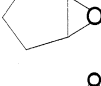
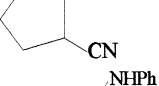
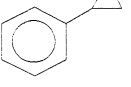
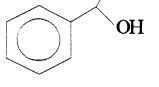
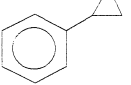
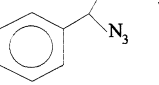
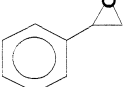
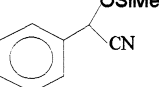
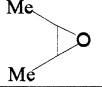
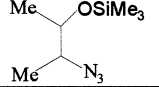
The Fe^{3+} content analysis of the catalyst was carried out as reported by Vogel [18]. We have investigated the ring opening reaction of cyclohexene oxide with aniline over different K10 montmorillonite catalysts (Table 1). It was observed that Fe pillared with K10 montmorillonite exhibited maximum activity. The efficiency of FePILC–K10 is evident from the high yields obtained for the nucleophilic ring opening reactions of oxiranes (Table 2). Such high yields simplify the procedure of separation of the product. The increased activity of FePILC–K10 was not only due to the Fe^{3+} content, but also due to another factor, the pillaring effect, with the hydroxy oligomers of the pillared clay playing a vital role.

This new methodology offers many advantages over the existing methodologies: (1) montmorillonite is cheaper and abundantly available in nature; (2) the reaction time is very short; (3) the catalytic reaction affords the trans products (entries 2, 5, 10) in good yields; (4) the conver-

Table 1
Ring opening reaction of cyclohexene oxide with aniline catalysed by different clay catalysts

S. No.	Catalyst	Fe_2O_3 (%)	Reaction time (h)	Isolated yield (%)
1	K10	4.62	36	50
2	Fe-exchanged K10 montmorillonite	6.32	4	79
3	FePILC–K10	12.34	1.5	95

Table 2
Ring opening of oxiranes by iron pillared clay

S. No.	Oxirane	Nucleophile	Product ^a	Reaction time (h)	Yields ^b (%)
1		PhNH ₂		1.5	95 ^c 95 ^{c,d}
2		TMSN ₃		2.0	~100
3		TMSCN		2.0	~100 89 ^c
4		PhNH ₂		2.0	~100 98 ^c
5		TMSN ₃		2.5	~100 65 ^c
6		TMSCN		2.5	~100 98 ^c
7		PhNH ₂		1.5	98 ^c
8		TMSN ₃		2.0	98 ^c
9		TMSCN		2.0	98 ^c
10		TMSN ₃		2.5	60 ^c

^a Products (1a–10a).

^b NMR yields.

^c Isolated yields.

^d Recovered catalyst.

sions are quantitative; (5) the work-up comprises of simple filtration; and (6) the recovered catalyst can be recycled without any further activation. In view of the above advantages, this process is of utmost potential in practical use.

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