Superactive Mg-Al-O-t-Bu Hydrotalcite for Epoxidation of Olefins

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Abstract: Epoxidation of unfunctionalised olefins and α , β -unsaturated ketones has been accomplished at an amazingly and unprecedented rate by superactive Mg-Al-O-t-Bu-hydrotalcite solid base catalyst prepared in our laboratory.

Hydrotalcites consist of Brucite-like layers having positive charge countered by anionic species intercalated to form neutral materials. The basicity and activity can be easily tuned up choosing a set of hetero elements, changing the element ratio, and anion species intercalated from a pool of wide range of multioptions.¹⁻³ Recently, the exquisite solid bases are of increased attention in view of their ubiquitous characteristics and are being considered for possible replacement of soluble bases in the base induced chemical processes to offer environmentally benign technologies.⁴⁻⁷

Epoxides are versatile building blocks for organic synthesis.⁸ Hydrotalcite carbonates as synthesised and the calcined samples have been probed for epoxidation of unfunctionalised and electron deficient olefins respectively and are found to be active.^{6, 9-12} However, the rates of the reactions are slow. We effected very recently modifications on hydrotalcites to induce aldol reactions successfully. Incorporation of *t*-butoxide in the interlayers of hydrotalcite by anion-exchange provided a simple methodology for the preparation of Mg-Al-O-t-Bu-hydrotalcite **[I]** for the selective synthesis of aldols.¹³

In the present endeavour, we describe a magnificent display of superactivity in the epoxidation of unfunctionalised as well as electron deficient olefins employing **I** as a base catalyst and hydrogen peroxide as an oxidant under a set of different conditions as described in schemes 1 and 2.



Scheme 1







Entry	Substrate	Rxn. time	Product	Yields (%) ^b
1		10 min		100 03 ^c
1		24 h ^d		93 97 ^d
		10 h		80 ^e
		12 h		85 ^f
2	H₃C-⟨◯)-OH=OH=C-⟨◯⟩	30 min	н₃с–⊖–сн–сн–с–⊖	100
3	ӊ∞–◯́–а⊨а⊢с́–◯́	45 min		53
4	ci()-cit=cit-()	15 min	CI-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-CH-	86
5	ол-O-at-at-c-O	10 min	o₂n-⊖-ch-ch-ch-(⊖)	88
6		5 min ^g 6 h ^d		90 92 ^d
7		5 min ^h	0	94

Table 1. The epoxidation of electron-deficient alkenes catalysed by Mg-Al-O-t-Bu hydrotalcite^a

^a All reactions were carried out with 30% H_2O_2 (0.35 ml), 1 mmol of substrate and 0.03g of catalyst [I] at room temperature in methanol. ^b Yields of epoxides determined by ¹H NMR based on olefins. ^c Isolated yield. ^d Results reported with calcined hydrotalcite ref. 6 using 0.150g of catalyst. ^e potassium *t*-butoxide as catalyst. ^f By separate addition of Mg-Al-NO₃ hydrotalcite and potassium *t*-butoxide. ^g Reaction conducted at 0⁰C using 0.005g of catalyst; 2160-fold activity compared with ref. 6. ^h Reaction conducted at 0⁰C using 0.005g of catalyst.

Table 2. The epoxidation of various unfunctionalised olefins catalysed by Mg-Al-O-t-Bu hydrotalcite^a.



^a All reactions were carried out with 30% H_2O_2 (2.4 ml), 4 mmol of olefin, 10.5 mmol of benzonitrile and 0.01g of catalyst at 60^oC in methanol. ^b Yields of epoxides determined by ¹H NMR based on olefins. ^c Isolated yield ^d Results reported with hydrotalcite carbonate [ref. 12] using 0.050g of catalyst.

1. **I** displayed amazing 720-fold activity over simple calcined hydrotalcite in the epoxidation of chalcone [entry 1]. Chalcones with electron-withdrawing groups flanked at para position [entries 4,5] are epoxidised faster than the chalcones possessing electron-donating groups [entries 2,3]. The catalyst **I** maintained its supremacy in the activity profile of epoxidation of other substrates, when compared with the results of calcined hydrotalcite reported.⁶ Under the conditions mentioned in scheme 1, epoxidation of unfunctionalised olefins remained inactive. The use of benzonitrile which gives peroxycarboximidic acid¹⁴ by the interaction of hydrogen peroxide however promoted the epoxidation reaction of unfunctionalised olefins with **I**. The results with catalyst **I** are compared with those of hydrotalcite carbonates of Kaneda *et al.*¹² in Table 2. **I** showed 720-fold activity over the best hydrotalcite carbonate [entry 1].

Interestingly, with potassium *t*-butoxide in place of **I**, the reaction [Table 1, entry 1] took 10 h to afford a reasonable yield of 80%. In a separate experiment [Table 1, entry 1] conducted by adding Mg-Al-NO₃ hydrotalcite and potassium *t*-butoxide to the reaction medium, the reaction afforded 85% conversion in 12h and there was no further

reaction even after prolonging the reaction time. This certainly indicates that *t*-butoxide ion is intercalated in the catalyst **I**. The epoxidation of terminal olefins to racemic epoxides in excellent yields is noteworthy and assumes further significance since value added optically pure epoxides and 1,2-diols could be easily obtained from the racemic epoxides through kinetic resolution.⁸

Therefore, the amazing activity of Mg-Al-O-t-Bu-Hydrotalcite catalyst in the epoxidation of various olefins is ascribed to the anion O-t-Bu paired with Mg and Al of the main frame hydrotalcite since the reaction was practically very slow with potassium *t*-butoxide and a mixture of potassium t-butoxide and Mg-Al-NO₃ hydrotalcite in separate experiments conducted under identical conditions. In other words, the intercalated anionic *tert*. butoxide species in conjunction with Mg and Al projected superactivity in the epoxidation reactions. In view of the superactivity expressed both in epoxidation of unfunctionalised and electron-deficient olefins, the present catalyst can be a potential candidate to offer environmentally benign chemical technologies.

Acknowledgement: We gratefully acknowledge the financial support of this work by Commission of the European Communities [CII*-CT94-0050 (DG12 HSMU)].

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