

## Aldol Condensations Catalysed by Novel Mg-Al-O-*t*-Bu Hydrotalcite

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**Abstract:** A novel Mg-Al-O-*t*-Bu hydrotalcite prepared for the first time, catalyses condensation reactions selectively to aldols (3) at 0°C in quantitative yields.

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There has been increasing attention on the design and use of environmentally compatible solid acid-base catalysts targeted to minimise the emission of effluents in chemical industries. These solid acid-base catalysts can be easily separated and recycled. Layered double hydroxides (LDHs) or hydrotalcite like compounds (HTLCs) have recently received considerable commercial interest<sup>1</sup> as adsorbents, anion exchangers and most important as base catalysts<sup>2-4</sup>. Hydrotalcites are represented by the formula  $[M^{2+}(1-x)M^{3+}x(OH)_2]x^+(A^{m-}x/m).nH_2O$ , where the  $M^{2+}$  are the divalent ions and  $M^{3+}$  are the trivalent ions. The compensating anions may be  $OH^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $CO_3^{2-}$  etc. and on their expulsion at 450°C, LDHs gives a highly active homogeneous mixed oxide which is potentially a basic catalyst for a variety of organic transformations such as aldol condensation<sup>5</sup>, olefin isomerization<sup>2</sup>, epoxidations of activated olefins with hydrogen peroxide<sup>6</sup>, alkylations of diketones<sup>7</sup>, nucleophilic halide exchange<sup>8</sup> and Claisen-Schmidt condensation<sup>9</sup> etc.

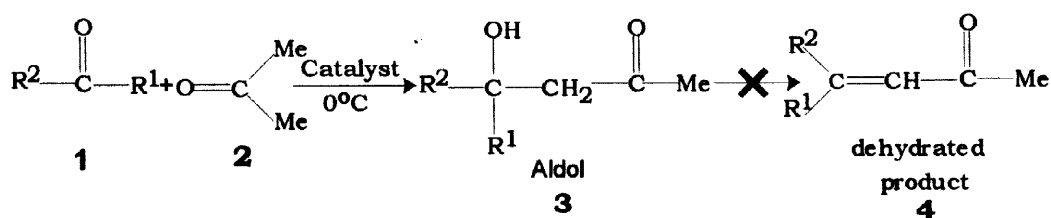
The aldol condensation is of prime importance for fine chemical synthesis and is generally catalysed by acids or bases<sup>10</sup>. In the laboratory, many catalysts have been reported such as alumina<sup>11,12</sup>, zeolites<sup>13</sup>, sepiolite<sup>14</sup>, and hydrotalcites<sup>9,15</sup>. The reported works<sup>5,7,15,16</sup> on aldolisations were performed at relatively high temperatures. Earlier, we designed and developed modified hydrotalcite by incorporation of hydroxyls during the rehydration process and found it to be excellent for aldol condensation<sup>17</sup>. Now, we opted a novel approach of incorporation of *tert*-butoxide by an exchange process, to tune up the hydrotalcite for higher basicity. We report in this letter the preparation of Mg-Al-O-*t*-Bu hydrotalcite and selective condensations to aldol products.

The catalyst was prepared from Mg-Al-NO<sub>3</sub> hydrotalcite by exchanging the NO<sub>3</sub><sup>-</sup> ions with O-*t*-Bu anions. Mg<sub>6</sub>Al<sub>2</sub>NO<sub>3</sub>-HT was synthesized as follows. To exclude CO<sub>3</sub><sup>2-</sup> ions, all solutions were prepared with CO<sub>2</sub>-free deionised water, and the syntheses were performed under a nitrogen atmosphere in a glovebox. Magnesium nitrate hexahydrate (30.8g, 0.12mol) and aluminium nitrate nonahydrate (15.0g, 0.04mol) were dissolved in 100ml of deionised and decarbonated water. The pH of the solution was adjusted to 10 by adding 2M NaOH. The resulting suspension was stirred for 2h at room temperature. The precipitated hydrotalcite was collected by filtration under N<sub>2</sub> atmosphere and dried overnight at 80°C. Mg-Al-O-*t*-Bu-HT was prepared from Mg-Al-NO<sub>3</sub>-HT (1.214g) by exchange with 0.1 M solution of potassium *tert*-butoxide in 100ml of THF under stirring at room temperature for 24h. The precipitate (Mg-Al-O-*t*-Bu-HT) was filtered under a N<sub>2</sub> atmosphere to yield 1.382g.

The Mg-Al-O-*t*-Bu-HT was tested as a base catalyst for aldol condensations (Scheme 1). Aldol products (**3**) were obtained selectively in quantitative yields under mild reaction conditions (Table 1). These results were quite impressive since the corresponding α,β-unsaturated carbonyl compounds (**4**) were the major products in earlier reports<sup>9,16</sup>.

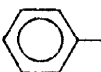
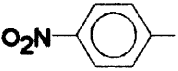
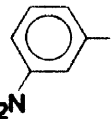
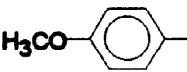
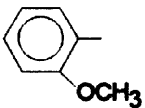
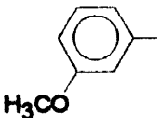
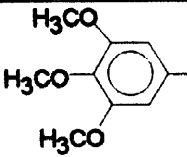
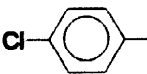
An attempt was done in order to check the stability and heterogeneity of *tert*-butoxide exchanged on hydrotalcite, using the following procedure: 50mg of Mg-Al-O-*t*-Bu-HT was added to 15ml of ether in a two necked flask. It was stirred at 0°C in N<sub>2</sub> atmosphere for about 1h. The slurry was filtered under nitrogen, then the regular reaction was carried separately with filtrate and the residue. While complete conversion was observed in the reaction carried out with residue, there was absolutely no conversion in the reaction carried out with the filtrate, even after 45min. It can therefore be concluded that the *tert*-butoxide is not simply adsorbed on hydrotalcite as on xonotlite<sup>18</sup>.

Scheme-1



R<sup>1</sup> = H (Entry 1-8, Table 1)

Table 1. Aldol condensations catalysed by Mg-Al-O- t-Bu hydrotalcite catalyst<sup>a</sup>.

Entry	R <sup>1</sup>	Time (min)	Conversion (%) <sup>b</sup>	Isolated Yields (%)
1		15	100	95 <sup>c</sup>
2		30	100	91
3		10	100	97
4		30	90	88
5		15	100	93
6		10	100	97
7		10	100	92
8		20	100	93

<sup>a</sup> All reactions were performed on 2mmol of aldehyde in 10ml acetone using 0.05g of catalyst at 0°C. <sup>b</sup>By <sup>1</sup>H NMR, based on aldehyde. <sup>c</sup>Compound: (entry 1) **PhCH(OH)CH<sub>2</sub>COCH<sub>3</sub>** shows <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 2.15 (s, 3H), 2.8 (d, 2H), 5.1 (m, 1H), 7.3 (m, 5H aromatic); IR (KBr pellets) 3440 cm<sup>-1</sup> (broad signal, OH), 1712 cm<sup>-1</sup> (sharp, C=O); MS (EI, 70 ev) m/z (RA) 164 (30), 146 (39), 131 (15), 107 (78), 105 (33), 79 (93), 77 (57), 58 (32), 43 (100). The remaining products were characterised similarly.

In conclusion, the exchange of hydrotalcite by *tert*-butoxide anions increases the activity manifold since the Claisen-Schmidt condensation of benzaldehyde and acetone, which afforded about 90% yield in aldol in 3 hours on an hydrotalcite first calcined, then rehydrated<sup>17</sup>, is now achieved with a similar efficiency in about 15min. This increase in activity is indicative of a deep modification of the basic properties of the solid accentuated by incorporation of *tert*-butoxide anion. This new solid catalyst offers a practical alternative to soluble bases in view of the following advantages, a) high catalytic activity under mild reaction conditions, b) easy separation of the catalyst after the reaction, c) selective formation of aldol product.

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#### References and notes

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