Hydrotalcites as catalysts for the Baeyer–Villiger oxidation of cyclic ketones with hydrogen peroxide/benzonitrile

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Abstract—Hydrotalcites (HTs) in variable Mg/Al ratios were used as catalysts for the Baeyer–Villiger (BV) oxidation of cyclic ketones with hydrogen peroxide. All HTs studied were found to be active in the BV oxidation of cyclohexanone, their activity increases with increasing Mg/Al ratio. The reaction, which was conducted under very mild conditions (viz. atmospheric pressure and a temperature of 70 °C), provided conversions above 70% with 100% selectivity only after 6 h. This outcome was found to require the presence of a nitrile in the reaction medium, so a mechanism involving adsorption of the nitrile and cyclohexanone onto the catalyst is proposed that is consistent with the experimental results. Based on the proposed mechanism, the presence of a surfactant should result in improved conversion and catalytic activity, as was indeed observed with sodium dodecylsulfate in the reaction medium. The best catalyst among those tested was used with other cyclic ketones and found to provide excellent conversion and selectivity results in most cases.
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1. Introduction

Hydrotalcite-like compounds, also known as layered double hydroxides, have aroused much interest by virtue of their potential uses in various scientific fields such as organic synthesis.[1–3] The structure of these compounds is based on that of a natural mineral called hydrotalcite,[4] which is a magnesium-aluminum hydroxycarbonate of formula Mg_6-$Al_2(OH)_{16}CO_3 \cdot 4H_2O$ structurally similar to brucite except for the fact that some Mg^{2+} ions have been replaced with Al^{3+}; this results in the presence of layers bearing positive charge that is countered by carbonate ions in the interlayer spacing. Replacing the magnesium, aluminum or both cations with another metal, or the carbonate with another anion, allows a large family of compounds known as hydrotalcite-like compounds (HTs) or layered double hydroxides (LDHs) of formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ to be obtained. In the formula, M(II) is a divalent cation such as Mg, Cu, Ni, Co, or Zn;[3] M(III) is a trivalent cation such as Al, Fe, Cr, V, Mn, Ga, or In;[3,5,6] A^{n-} is the charge-balancing anion, which can be organic or inorganic and widely variable in nature; and x=M(III)/[M(II)+M(III)].

In this work, we synthesized HTs in variable Mg/Al ratios for use as catalysts in the Baeyer–Villiger oxidation of

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cyclohexanone. This reaction was first employed in 1899 by Baeyer and Villiger to convert ketones into esters.[7] Since then, it has become a very important tool for organic synthesis, and been the subject of a number of books and of both dedicated[8–12] and general organic oxidation reviews.[13,14] Currently, the Baeyer–Villiger reaction involves the oxidation of ketones with organic peroxyacids or alkyl hydroperoxides to obtain esters (or lactones) or, alternatively, alcohol or acid derivatives. The reaction also includes the oxidation of aldehydes to the corresponding esters of formic acid or their hydrolysis products. The accepted mechanism for this process involves two steps (see Scheme 1), namely: addition of the peroxyacid to the carbonyl compound to form a Criegee adduct (**1**) and rearrangement of the adduct to the reaction end-product (**2**). The migration of group R' occurs in a concerted manner with the cleavage of the O–O bond. The rearrangement step is facilitated by the presence of bases, which helps to remove the hydroxyl proton from the Criegee
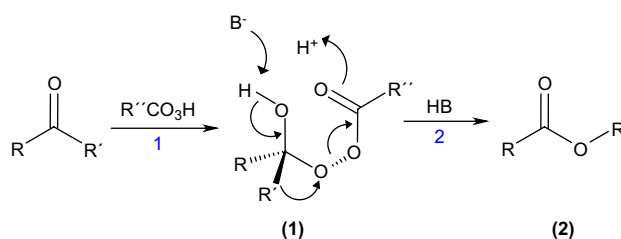
Scheme 1. General mechanism for the Baeyer–Villiger oxidation of ketones with organic peracids.

intermediate. The Baeyer–Villiger oxidation of ketones provides a number of advantages such as: (a) a high tolerance to the presence of a variety of functional groups in the substrate (thus, peracids usually attack the carbonyl group in an unsaturated ketone as long as the double bond is not conjugated), (b) regiochemical selectivity control via the migration ability of various groups (with some compounds such as bicyclic systems, the oxygen insertion regioselectivity can be influenced by specific stereoelectronic factors, however), and (c) the ability to use a wide variety of oxidants.

Ti-silicalite (TS-1) was one of the catalysts that revolutionized the field of organic oxidations. This solid consists of a zeolite structure (silicalite) into which titanium is incorporated.[15] Its high oxidizing power lies in the ability of titanium metal sites to form Ti-peroxy species that can activate hydrogen peroxide in various oxidation reactions including epoxidations, ammonoxidations, and CH oxidations.[16,17] These catalysts have been further developed by inserting new oxidizing metals into zeolite structures, albeit with poorer results than those originally obtained with titanium. However, Corma et al. developed a catalyst consisting of Sn incorporated into a beta zeolite that has provided results comparable to those of TS-1 in processes involving the activation of hydrogen peroxide in some step.[18] In subsequent work,[19–24] Corma et al. conducted extensive research into Baeyer–Villiger oxidation reactions using their Sn-beta zeolite catalysts. Recently, they proposed a mechanism for the underlying process from a combination of theoretical and experimental data;[25] according to it, tin, which acts as an oxygen transfer agent, activates the carbonyl group in cyclohexanone.

As noted earlier, in this work we tested various HT-based heterogeneous catalysts in combination with hydrogen peroxide as oxidant in the Baeyer–Villiger oxidation reaction. In previous work, our group found HTs to be effective catalysts for reactions requiring the presence of a base (e.g., the epoxidation of limonene with hydrogen peroxide[26,27] or the Meerwein–Ponndorf–Verley reaction).[28–32] Other authors have also previously used HTs as catalysts for the BV reaction, albeit with a mixture of molecular oxygen and benzaldehyde[33,34] or a peroxyacid[35] as oxidant. Also, a hydrotalcite-supported SnO_2 catalyst was found to effect the BV reaction with hydrogen peroxide as oxidant in the presence of a nitrile as oxygen transfer agent.[36]

2. Results and discussion

2.1. Characterization of catalysts

2.1.1. Elemental analysis.
Table 1 shows the chemical composition and empirical formula of each HT used as

determined by ICP-MS. The experimentally determined values were quite consistent with their theoretical counterparts, the differences falling within the experimental error range.

2.1.2. XRD results.
Figure 1 shows the XRD patterns of the studied HTs. As can be seen, they exhibit the typical signals for hydrotalcite,[37] with tall, sharp, symmetric peaks for the planes (003), (006), (110), and (113), and broad, somewhat less symmetric peaks for the planes (009), (015), and (016), all of which are typical of the layered clay minerals.
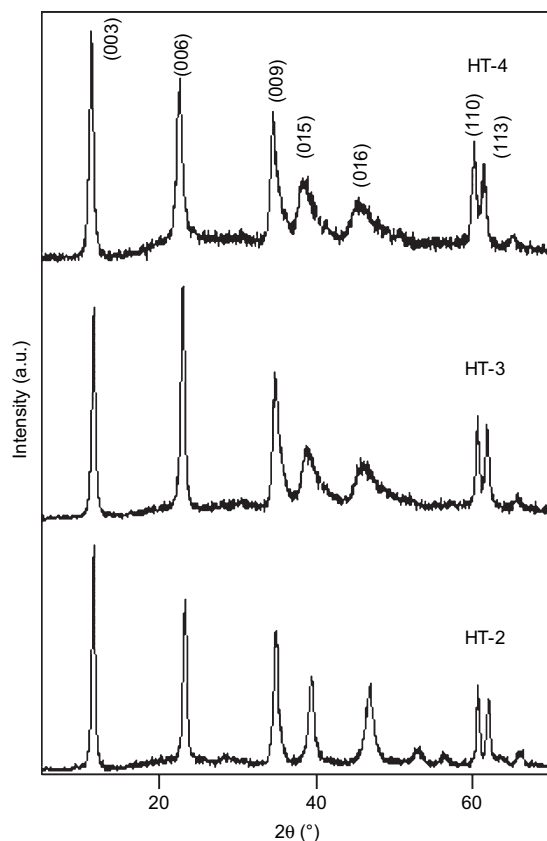

Figure 1. XRD patterns for the HTs synthesized.

Table 1 gives the lattice parameters a and c as determined from the XRD patterns [$a=2\times d_{(110)}$ and $c=3\times d_{(003)}$]. Parameter a can be likened to the distance between two adjacent ions in a brucite-like layer; based on Table 1, a increased with decreasing metal ratio x [$x=Al/(Mg+Al)$] or increasing Mg/Al ratio. These results are consistent with an increase in the proportion of trivalent cation (aluminum)

Table 1. Metal ratios, chemical formulae, and lattice parameters for the HTs

Catalyst	x_{ther}[a]	x_{exp}[b]	Chemical formulae[c]	a[d] (Å)	c[d] (Å)
HT-2	0.33	0.37	$Mg_{0.631}Al_{0.369}(OH)_2(CO_3)_{0.185}\cdot0.65H_2O$	3.046	22.860
HT-3	0.25	0.29	$Mg_{0.710}Al_{0.290}(OH)_2(CO_3)_{0.145}\cdot0.61H_2O$	3.052	22.878
HT-4	0.20	0.22	$Mg_{0.779}Al_{0.211}(OH)_2(CO_3)_{0.110}\cdot0.60H_2O$	3.068	23.421

[a] Theoretical metal ratio [$x=Al/(Mg+Al)$].
[b] Experimental metal ratio as determined by ICP-MS.
[c] Crystallization water was quantified by thermogravimetric analysis.
[d] Lattice parameters.