Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 62 (2006) 11697–11703
Tetrahedron

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

José Rafael Ruiz,* César Jiménez-Sanchidrián* and Rafael Llamas

Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie. Carretera Nacional IV-A, km. 396, 14014 Córdoba, Spain

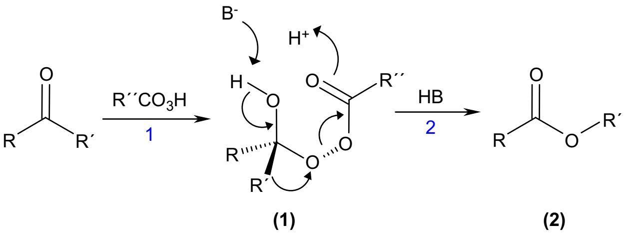
Received 16 August 2006; revised 12 September 2006; accepted 13 September 2006

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.

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 $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$ 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 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.

Keywords: Hydrotalcite; Baeyer–Villiger oxidation; Cyclic ketones; Hydrogen peroxide.

* Corresponding authors. Tel.: +34 957 218638; fax: +34 957 212066; e-mail: qo1ruarj@uco.es

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.09.044

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.

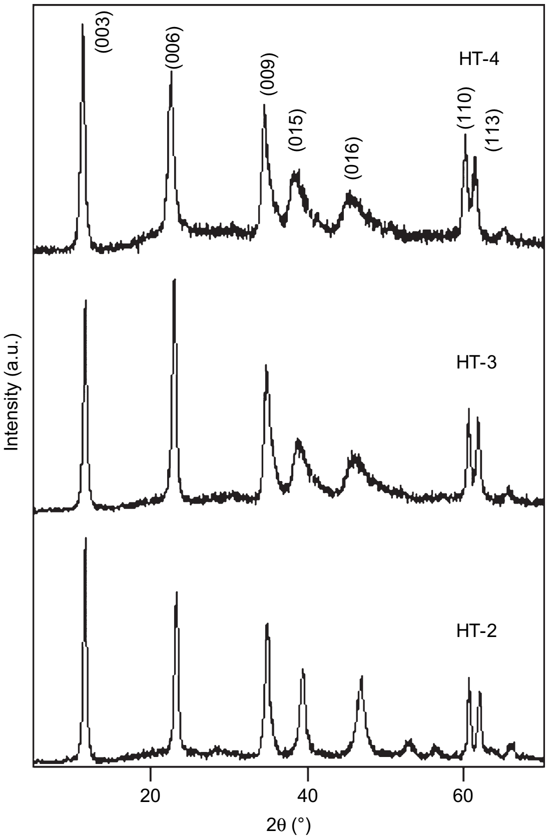


Figure 1. XRD patterns for the HTs synthesized.

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	$Mg_{0.631}Al_{0.369}(OH)_2(CO_3)_{0.185}\cdot 0.65H_2O$	3.046	22.860
HT-3	0.25	0.29	$Mg_{0.710}Al_{0.290}(OH)_2(CO_3)_{0.145}\cdot 0.61H_2O$	3.052	22.878
HT-4	0.20	0.22	$Mg_{0.779}Al_{0.211}(OH)_2(CO_3)_{0.110}\cdot 0.60H_2O$	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.

increasing in the distance between cations in the brucite-like layers.[38] In addition, parameter c increased with decreasing metal ratio x; although its relationship to such a ratio is unclear, it usually exhibits the observed trend.[38]

2.1.3. Textural properties. Table 2 lists the specific surface area, average pore diameter, and pore volume of the HTs, all of which fall within the usual ranges for this type of solid.

Table 2. Specific surface area, pore volume, and average pore diameter of the synthesized solids and their calcination products

Catalyst	S_{BET} (m^2/g)[a]	V_p (mL/g)[b]	d_p (Å)[c]
HT-2	65.2	166.9	0.59
HT-3	72.4	169.8	0.62
HT-4	75.8	158.8	0.74

[a] Specific surface area.
[b] Pore volume.
[c] Average pore diameter.

The nitrogen adsorption–desorption isotherms were similar for the three HTs. By way of example, Figure 2 shows that for solid HT-4. All isotherms were of type II in the IUPAC classification[39] and exhibited a hysteresis cycle closing at ca. 0.8 (P/P_0) of type H3 in the de Boer classification;[40] therefore, the samples were mesoporous or macroporous and contained no micropores. The fact that the adsorption and desorption branches of the isotherms are nearly parallel suggests the presence of pores of regular geometry; also, the high slopes of the desorption branch suggest that the pore dimensions span a narrow range.[41]

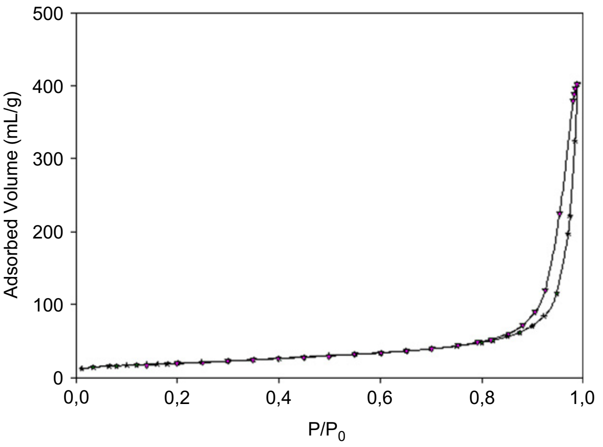


Figure 2. Nitrogen adsorption–desorption for sample HT-4.

2.2. Baeyer–Villiger oxidation

2.2.1. Catalytic activity. The Baeyer–Villiger oxidation under the reaction conditions used is a complex process as regards both the reactants, the catalysts and the resulting products. It is thus crucial to determine the role played by each reactant as a function of its nature and concentration. This entails conducting a series of kinetic tests ensuring a constant behavior in the reactants with time. The overall process can be fitted to a general kinetic equation such as

$$v = k[\text{cyclohexanone}][H_2O_2][\text{benzonitrile}]$$

which contains a concentration term for each reactant. This involves the unsurmountable difficulty of mixing arising from the low aqueous solubility of the organic products over some concentration ranges. We thus chose to conduct our experiments under reaction conditions where the orders with respect to H_2O_2 and the benzonitrile used would be zero, so the overall kinetic equation could simplify to

$$v = k'[\text{cyclohexanone}]$$

and the results obtained would only be a consequence of changes in the cyclohexanone conversion. Consequently, the experiments described below were carried out in excess H_2O_2 and benzonitrile relative to the stoichiometric amounts.

Catalytic activity experiments were preceded by blank tests intended to ascertain that the reaction developed to no appreciable extent in the absence of the catalyst and that the presence of a nitrile was essential. As can be seen from Table 3 (entries 7 and 8) the reaction did not develop in the absence of catalyst or benzonitrile.

Table 3. Conversion to ε-caprolactone in the Baeyer–Villiger oxidation of cyclohexanone

Entry	Catalyst	Conversion (%)[a]	t (h)[b]	r_a (mmol/h)[c]
1	HT-2	71	6	6.6
2	HT-3	74	6	7.1
3	HT-4	88	6	8.0
4	HT-4-reused-1	89	6	7.8
5	HT-4-reused-2	87	6	8.0
6	HT-4-reused-3	88	6	7.9
7	Without catalyst	0	24	0
8	Without benzonitrile	0	24	0

[a] Conversion to ε-caprolactone.
[b] Reaction time.
[c] Initial catalytic activity (mmol of ε-caprolactone/h).

Table 3 lists the conversion values obtained at different reaction times and the initial catalytic activity. The latter was determined from the slope of the temporal variation of the conversion to ε-caprolactone, which was linear at low conversion levels. Based on the results, the initial catalytic activity of the studied solids increased with increasing Mg/Al ratio.

2.2.2. Catalyst reuse. Calcining a hydrotalcite above 350 °C destroys the layered structure by conversion into a mixed oxide Mg(Al)O_x.[5] However, the hydrotalcite structure can be recovered from solids calcined at 400–800 °C. We thus exploited this memory effect to reuse the catalyst. For this purpose, the solid was calcined at 450 °C and treated with a sodium carbonate solution to recover the layered structure following filtration of the reaction mixture. Based on the catalytic activity and conversion results obtained (Table 3), the catalyst exhibited no appreciable loss of activity after three reuses.

2.2.3. Mechanism of the process. Scheme 2 shows the proposed mechanism for the Baeyer–Villiger oxidation of ketones over HT catalysts. The process takes place in two steps. In the first, hydrogen peroxide attacks a Brönsted basic site on the catalyst surface to form a hydroperoxide species that subsequently attacks benzonitrile to give a peroxycarboximidic acid intermediate. This step is similar to that generally accepted for the epoxidation of alkenes with hydrogen peroxide over basic catalysts in the presence of nitriles or amides.[28,42] In the second step, the intermediate attacks the ketone, adsorbed at a Lewis acid site in the catalyst, to form an intermediate equivalent to the Criegee adduct in homogeneous catalysis processes that subsequently undergoes rearrangement to the final lactone. Corma et al.[18] reported a similar mechanism for the Baeyer–Villiger reaction with hydrogen peroxide over Sn-beta zeolite catalysts, where the carbonyl compound was adsorbed at Sn acid sites. These authors confirmed their mechanism via tests involving ^{18}O isotopic labeling, IR spectroscopy, and GC–MS and theoretical studies.[25]

If the proposed mechanism is accepted then the Baeyer–Villiger oxidation occurs at the interface between the organic and aqueous phases in the reaction medium, cyclohexanone and benzonitrile being in the organic phase, and hydrogen peroxide and the catalyst in the aqueous phase. Accordingly, the presence of a surfactant should expedite the reaction by both increasing the contact surface area between the two phases, and favoring the transfer of a lipophilic ketone from the organic phase to the interface. In order to confirm these assumptions, we conducted the reaction under the same conditions except for the presence of an amount of 0.6 mmol of surfactant in the medium. Both sodium dodecylsulfate (DS) and dodecylbenzenesulfonate (DBS) resulted in improved conversion and catalytic activity while preserving 100% selectivity. Figure 3 illustrates the favorable effect of the addition of a surfactant on the reaction rate; as can be seen, DS provided better results than DBS.

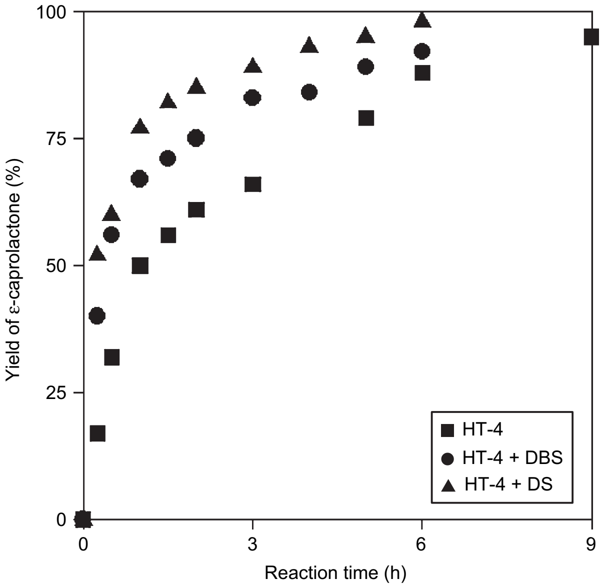
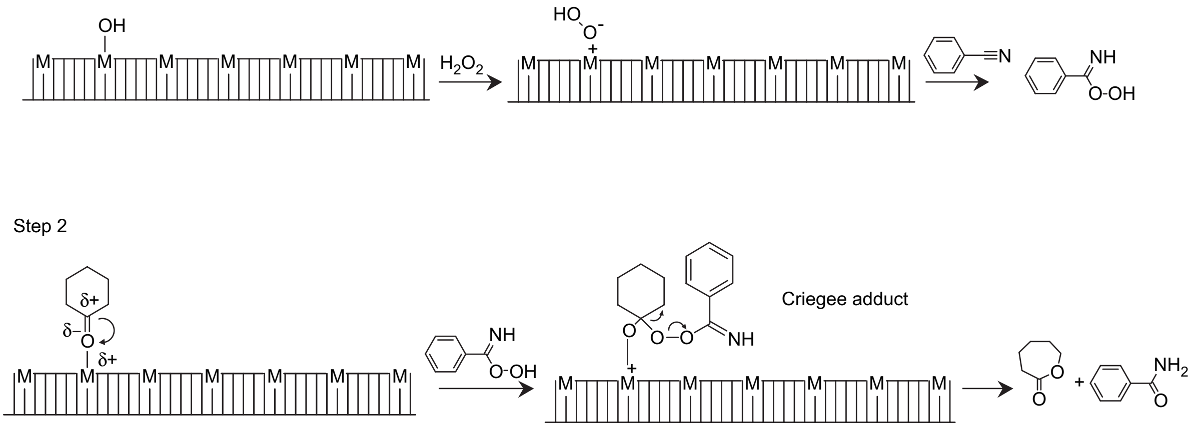


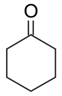
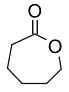
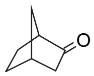
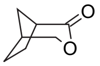
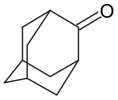
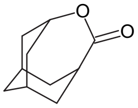
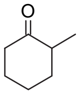
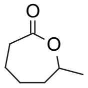
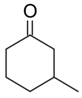
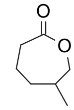
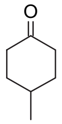
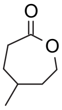
Figure 3. Reaction profile of the Baeyer–Villiger oxidation of cyclohexanone catalyzed with HT-4 with and without surfactants. Reaction conditions: cyclohexanone (12 mmol), benzonitrile (98 mmol), catalyst HT-4 (250 mg), 30% H_2O_2 (4 mequiv), surfactant (0.6 mmol), T=70 °C.

2.2.4. Oxidation of other cyclic ketones. The best catalyst among those studied was tested on other cyclic ketones in order to assess its efficiency. As can be seen in Table 4, the conversion after 6 h of reaction was always equal or close to 100%. With substituted methylcyclohexanones, the initial catalytic activity decreased in the sequence from that with the methyl group at position 4 to that with the group at position 2. These results are consistent with the proposed mechanism. In fact, the presence of a methyl substituent in cyclohexanone must hinder the adsorption of the catalyst and hence the formation of the Criegee adduct; because position 2 was the most sterically hindered, the corresponding methylcyclohexanone was the one that exhibits the lowest catalytic activity values among the three. Similar arguments can be used with adamantanone and norcamphor. Also, the fact that 2- and 3-methylcyclohexanones exhibited less than 100% selectivity can be ascribed to their asymmetry



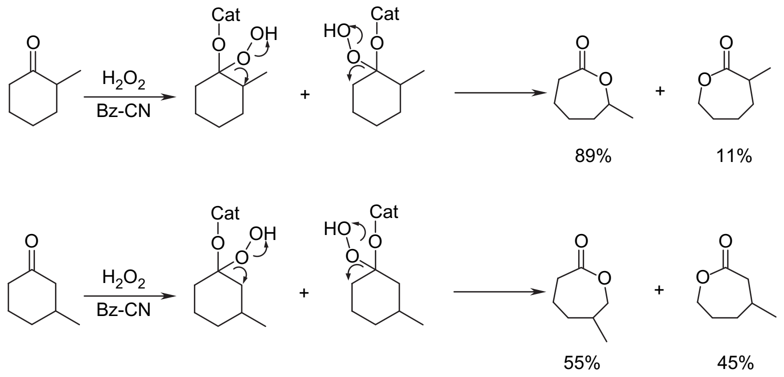
Scheme 2. Proposed mechanism for the Baeyer–Villiger oxidation of cyclohexanone over HTs.

Table 4. Conversion obtained in the Baeyer–Villiger oxidation of various saturated cyclic ketones with hydrogen peroxide over solid HT-4 as catalyst

Entry	Substrate	Product	Conversion (%)[a]	Selectivity (%)[b]	t (h)[c]	r_a (mmol/h)[d]
1			100	100	6	25.1
2			100	100	6	16.1
3			89	100	6	11.8
4			90	89	6	12.8
5			96	55	6	16.7
6			95	100	6	17.8

[a] Conversion to lactone.
[b] Selectivity to lactone.
[c] Reaction time.
[d] Initial catalytic activity (mmol of ε-caprolactone/h).

allowing the formation of two different lactones. With 2-methylcyclohexanone, the selectivity for the desired product (entry 4 in Table 4) was close to 90% by virtue of the migrating ability being more favorable in a tertiary carbon than in a secondary one. With 3-methylcyclohexanone (entry 5 in Table 4), however, the selectivity was close to 50% by effect of the migrating ability of the two methylene groups in α with respect to the carbonyl carbon being similar. Scheme 3 is consistent with the previous reasoning.



Scheme 3. Criegee adducts proposed as intermediates in the Baeyer–Villiger oxidation of 2- and 3-methylcyclohexanones.

3. Conclusions

We synthesized hydrotalcite-like compounds in variable Mg/Al ratios and used them in the Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide, where they exhibited good catalytic activity and selectivity toward ε-caprolactone. Their catalytic activity was found to increase with increasing magnesium content in the solid. These results are consistent with a mechanism involving the adsorption of hydrogen peroxide at a Brönsted basic site in the catalyst to form a peroxycarboximidic acid intermediate with benzonitrile that effects the transfer of oxygen to cyclohexanone adsorbed at a Lewis acid site in the catalyst. The solids were found to retain their catalytic activity after three reuses. Based on the proposed mechanism, the presence of a surfactant in the reaction medium should increase the conversion. This was indeed the case with sodium dodecylbenzenesulfonate and, especially, sodium dodecylsulfate. Finally, the best catalyst among those studied also proved effective in the oxidation of other cyclic ketones, with excellent conversion and selectivity results.

4. Experimental

4.1. General

$Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, and H_2O_2 (about 30%) were purchased from Panreac. Cyclic ketones, nitriles, and surfactants were purchased from Aldrich and used without further purification. All of the oxidation products were identified by mass spectrometry.

4.1.1. General procedure for the preparation of hydrotalcite-like compounds. The HTs were prepared from solutions of $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ in Mg(II)/Al(III) ratio=2, 3, and 4 using a coprecipitation method described elsewhere.[5] In a typical synthetic run, a solution containing 0.3 mol of $Mg(NO_3)_2\cdot 6H_2O$ and 0.15 mol of $Al(NO_3)_3\cdot 9H_2O$ in 250 mL of de-ionized water was used. This solution was slowly dropped over 500 mL of Na_2CO_3 solution at pH 10 at 60 °C under vigorous stirring. The pH was kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was kept at 80 °C for 24 h, after which the solid was filtered and washed with 2 L of de-ionized water. The HTs with Mg(II)/Al(III) ratios=3 and 4 were obtained by following the same procedure, using appropriate amounts of the Mg(II) and Al(III) nitrates.

The HTs thus prepared were ion-exchanged with carbonate to remove ions intercalated between layers. The procedure involved suspending the solids in a solution containing 0.345 g of Na_2CO_3 in 50 mL of bidistilled, de-ionized water per gram of HT at 100 °C for 2 h. Then, each solid was filtered off in vacuo and washed with 200 mL of bidistilled, de-ionized water. The HTs thus obtained were subjected to a second ion-exchange operation under the same conditions. The exchanged HT solids were named HT-2, HT-3, and HT-4, indicating a Mg/Al ratio=2, 3, and 4, respectively.

4.1.2. Experimental techniques. The HTs obtained were characterized by using various instrumental techniques.

The metal contents in the catalysts were determined by inductively coupled plasma-mass spectrometry on a Perkin–Elmer ICP-MS instrument under standard conditions.

X-ray diffraction (XRD) analysis was performed in all catalysts in order to check for crystallinity. Powder patterns were recorded on a Siemens D-5000 diffractometer using Cu $K\alpha$ radiation. Scans were performed over the 2θ range from 5 to 70°, using a resolution of 0.02° and a count time of 2 s at each point.

Thermogravimetric analysis was performed on a Setaram Setsys 12 instrument by heating in an argon atmosphere from 25 to 800 °C at a 10 °C/min rate.

BET surface areas, pore diameter, and pore volumes were calculated from nitrogen adsorption–desorption isotherms that were obtained at −196 °C using a Micromeritics ASAP 2010 instrument. Samples were outgassed in vacuo at 100 °C for 12 h prior to use.

4.1.3. General procedure for the Baeyer–Villiger oxidation with hydrotalcites. Baeyer–Villiger oxidations runs were performed at 70 °C in a two-mouthed flask containing 12 mmol of cyclohexanone, 98 mmol of benzonitrile, 4 mequiv of hydrogen peroxide and 250 mg of catalyst. One of the flasks' mouth was fitted with a reflux condenser and the other was used for sampling at regular intervals. The system was shaken throughout the process. Products were identified from their retention times as measured by GC–MS analysis on an HP 5890 GC instrument furnished with a Supelcowax 30 m×0.32 mm column and an HP 5971 MSD instrument.

Acknowledgements

The authors gratefully acknowledge funding by Spain's Ministerio de Educación y Ciencia, Fondos Feder and to the Consejería de Innovación, Ciencia y Empresa de la Junta de Andalucía.

References and notes

1. Vaccari, A. *Appl. Clay Sci.* **1999**, *14*, 161–198.
2. Sels, B. F.; De Vos, D. E.; Jacobs, P. A. *Catal. Rev.—Sci. Eng.* **2001**, *43*, 443–488.
3. Cavanni, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *2*, 173–301.
4. Miyata, S. *Clays Clay Miner.* **1975**, *23*, 369–375.
5. Aramendia, M. A.; Avilés, Y.; Borau, V.; Luque, J. M.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *J. Mater. Chem.* **1999**, *9*, 1603–1607.
6. Aramendia, M. A.; Borau, V.; Jimenez, C.; Luque, J. M.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *Mater. Lett.* **2000**, *43*, 118–121.
7. Baeyer, A.; Villiger, V. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 3625–3627.
8. Hassal, C. H. *Org. React.* **1957**, *9*, 73–74.
9. Krow, G. R. *Org. React.* **1993**, *42*, 251–252.
10. Krow, G. R. *Tetrahedron* **1981**, *37*, 2697–2702.
11. Strukul, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 1198–1209.
12. Renz, M.; Meunier, B. *Eur. J. Org. Chem.* **1999**, 737–750.
13. Plesnicar, B. *Oxidation in Organic Chemistry*; Trahanosky, W. S., Ed.; Academic: New York, NY, 1978; p 254.
14. Hudlicky, M. *Oxidations in Organic Chemistry*; American Chemical Society: Washington, DC, 1990; p 186.
15. Taramasso, M.; Perego, G.; Notari, B. U.S. Patent 4,410,501, 1983.
16. Corma, A.; García, H. *Chem. Rev.* **2002**, *102*, 3837–3892.
17. Corma, A.; García, H. *Chem. Rev.* **2003**, *103*, 4307–4365.
18. Corma, A.; Nemeth, L. T.; Renz, M.; Valencia, S. *Nature* **2001**, *412*, 423–425.
19. Renz, M.; Blasco, T.; Corma, A.; Fornés, V.; Jensen, R.; Nemeth, L. *Chem.—Eur. J.* **2002**, *8*, 4708–4717.
20. Corma, A.; Navarro, M. T.; Renz, M. *J. Catal.* **2003**, *219*, 242–246.
21. Corma, A.; Fornés, V.; Iborra, S.; Mifsud, M.; Renz, M. *J. Catal.* **2004**, *221*, 67–76.
22. Corma, A.; Iborra, S.; Mifsud, M.; Renz, M.; Susarte, M. *Adv. Synth. Catal.* **2004**, *346*, 257–262.
23. Boronat, M.; Concepción, P.; Corma, A.; Renz, M.; Valencia, S. *J. Catal.* **2005**, *234*, 111–118.

24. Corma, A.; Iborra, S.; Mifsud, M.; Renz, M. *J. Catal.* **2005**, *234*, 96–100.
25. Boronat, M.; Corma, A.; Renz, M.; Sastre, G.; Viruela, P. M. *Chem.—Eur. J.* **2005**, *11*, 6905–6915.
26. Aramendia, M. A.; Borau, V.; Jiménez, C.; Luque, J. M.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *Appl. Catal., A: Gen.* **2001**, *216*, 257–265.
27. Aramendia, M. A.; Borau, V.; Jiménez, C.; Luque, J. M.; Marinas, J. M.; Romero, F. J.; Ruiz, J. R.; Urbano, F. J. *Stud. Surf. Sci. Catal.* **2000**, *130*, 1667–1672.
28. Aramendia, M. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *Appl. Catal., A: Gen.* **2001**, *206*, 95–101.
29. Aramendia, M. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *J. Mol. Catal., A: Chem.* **2001**, *171*, 153–158.
30. Aramendia, M. A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J. *Appl. Catal., A: Gen.* **2003**, *255*, 301–308.
31. Ruiz, J. R.; Jiménez-Sanchidrián, C.; Hidalgo, J. M.; Marinas, J. M. *J. Mol. Catal., A: Chem.* **2006**, *246*, 190–195.
32. Jiménez-Sanchidrián, C.; Hidalgo, J. M.; Ruiz, J. R. *Appl. Catal., A: Gen.* **2006**, *303*, 23–28.
33. Kaneda, K.; Ueno, S. *ACS Symp. Ser.* **1996**, *638*, 300–318.
34. Ueno, S.; Ebitani, K.; Ookubo, A.; Kaneda, K. *Appl. Surf. Sci.* **1997**, *121–122*, 366–371.
35. Kaneda, K.; Yamashita, T. *Tetrahedron Lett.* **1996**, *37*, 4555–4558.
36. Pillai, U. R.; Sahle-Demessie, E. *J. Mol. Catal., A: Chem.* **2003**, *191*, 93–98.
37. JCPDS X-ray Powder Diffraction File no. 22-700, 1986.
38. Brindley, G. W.; Kikkawa, K. *Neues Jahrb. Miner. Monatsh.* **1967**, 137–141.
39. Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R.; Rouquerol, J.; Sieminiewska, J. *Pure Appl. Chem.* **1985**, *57*, 69–74.
40. Greegs, S. J.; Sing, K. S. W. *Adsorption Surface Area and Porosity*; Academic: New York, NY, 1967.
41. Malherbe, F.; Forano, C.; Besse, J. P. *Microporous Mater.* **1997**, *10*, 67–84.
42. Yamaguchi, K.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **1999**, *64*, 2966–2968.