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The Baeyer–Villiger reaction on heterogeneous catalysts

César Jiménez-Sanchidrián, José Rafael Ruiz*

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

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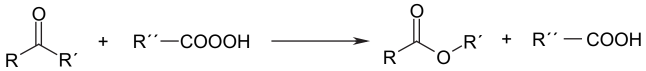
1. Introduction

The chemical reaction by which an alicyclic ketone is converted into an ester or a cyclic ketone by oxidation with a hydroxyacid (Scheme 1) was discovered by Baeyer and Villiger in the late 19th century.[1] The reaction, which was named after its discoverers, was subsequently extended to the oxidation of aldehydes to esters or their hydrolysis products with other reagents such as organic peracids and peroxides and hydrogen peroxide, among other oxidants.



Scheme 1. General scheme of Baeyer–Villiger reaction.

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* Corresponding author. Tel.: +34 957 218638; fax: +34 957 212066.
E-mail address: qo1ruarj@uco.es (J.R. Ruiz).

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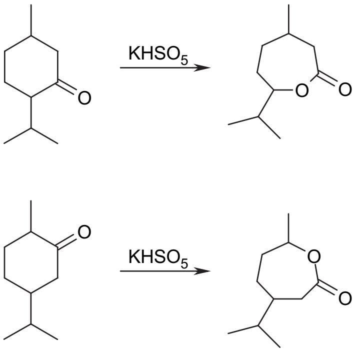
The original reaction studied by Baeyer and Villiger involved the formation of the lactones of mentone and carvomentone by treatment with a mixture of potassium monopersulfate and sulfuric acid (viz. Caro's acid) in the absence of solvent (Scheme 2). Since then, the reaction has been the subject of much study and widely documented.[2–8] This review focusses on heterogeneous catalysis in the Baeyer–Villiger reaction, with special emphasis on the variety of catalysts used. It should be borne in mind that catalytic methods currently provide a number of advantages over traditional stoichiometric methods, ranging from simpler operating conditions to the use of more inexpensive reagents and greater environmental friendliness (a result of the use and production of minimal amounts of toxic products and by-products, if any). The Baeyer–Villiger reaction has aroused much interest in synthetic organic chemistry as a powerful tool for such purposes as the preparation of natural products (e.g., antibiotics, steroids, pheromones) or monomers for polymerization processes, among many others.



Scheme 2. Reaction originally studied by Baeyer and Villiger,[1] which involved oxidation with potassium monopersulfate.

2. Mechanism of the Baeyer–Villiger reaction

The mechanism of the Baeyer–Villiger reaction was first elucidated by Criegee nearly 60 years ago and remains essentially unchanged today.[9] In fact, the currently accepted mechanism involves two steps similar to those initially proposed by Criegee (Scheme 3). In the first step the carbonyl group in the substrate (**1**) undergoes the nucleophilic attack of a peroxide species (**2**) to give a tetrahedral species (**3**) (Criegee intermediate), which subsequently rearranges to the corresponding ester (**4**) by migration of a hydrocarbon group simultaneously with the formation of a carboxylic acid molecule (**5**) from the peracid used.

The overall rate of the reaction is determined by that of the second step, which involves the migration of an alkyl group. In fact, as suggested by Benson and Suzuki already in 1959,[10] this step takes place in a concerted manner. With most reagents, the two steps are subjected to a similar energy of activation and therefore, catalysts can be expected to facilitate both, even though the rearrangement step is rate determining,[11] except in a few cases.[12]

Studies involving various hydrocarbon groups bonded to the carbonyl carbon have allowed the following sequences of migration ease to be established: tertiary alkyl>secondary alkyl>primary alkyl>methyl;[11] and *tert*-alkyl>cyclohexyl>*sec*-alkyl>benzyl>phenyl>*n*-alkyl>cyclopentyl>methyl.[4] These sequences are consistent with the increased electron-withdrawing[3] or migration-accelerating ability[11] of the bulkier groups. However, both can be altered by some conformational, steric and electronic factors. Thus, treating a phenylalkyl ketone with trifluoroperoxyacetic acid causes migration of the phenyl group in the ketone if the alkyl group is a primary group, but favours migration of the alkyl group if it is a secondary group.[11] However, the general protocol of the Baeyer–Villiger reaction is subjected to several constraints arising from the use of organic peracids. Two such constraints are related by the formation of 1 equiv of the corresponding carboxylic acid, or its salt, which must be re-used or discarded, and to the usually high cost and hazardous nature of peracids, which restricts their commercial use. These constraints have promoted research aimed at the in situ generation of organic peracids by reacting an aldehyde with molecular oxygen or a carboxylic acid with hydrogen peroxide.

For the migration of the group R′ in Scheme 3 to occur, the group must be in an antiperiplanar conformation with respect to both the O–O bond in the leaving group (primary stereoelectronic effect) and the electron pair on the OH group (secondary electronic effect) (see Fig. 1).[6]

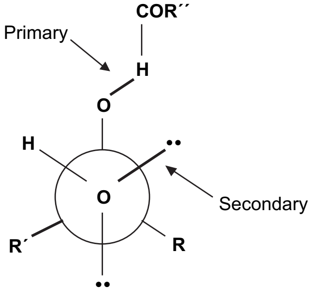
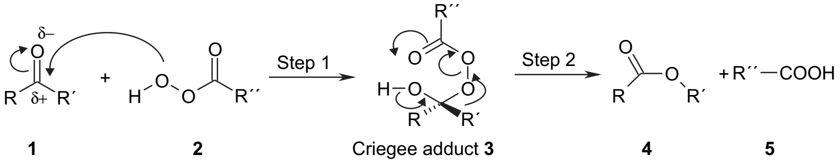


Figure 1. Spatial arrangement required for group R′ in Criegee adduct to migrate.



Scheme 3. Generally accepted mechanism for Baeyer–Villiger reaction of carbonyl compound with peracid.

3. Chemical methods and reagents for the Baeyer–Villiger reaction

The oxidants most commonly used in the Baeyer–Villiger reaction are *m*-chloroperbenzoic, trifluoroperacetic, perbenzoic and peracetic acids. A number of other acids have also been employed for this purpose, the oxidizing power of which is related to the conjugated addition power of the leaving group. Studies have allowed the following sequence of oxidizing power to be established for the acids typically used in the reaction: trifluoroperacetic>monopermaleic>mono-*o*-perphthalic>*p*-nitroperbenzoic>performic≈*m*-chloroperbenzoic>perbenzoic>peracetic≫perbutanoic.[3] Some of these acids must be handled with extreme care—particularly on a large operational scale—owing to their high intrinsic instability. This has led to their gradual replacement with more chemically stable oxidants such as bis(trimethylsilyl) peroxide[13] and magnesium monoperphthalate.[14,15] However, many of these oxidants exhibit poor selectivity in the Baeyer–Villiger reaction as they can attack other functional groups including alkenes, amines, phosphines and sulfides. This has promoted a search for alternative, chemoselective oxidants such as molecular oxygen and the use of new schemes based on homogeneous or heterogeneous catalysts including metals, metal complexes, oxides and salts. In addition, the reaction can be catalyzed by enzymes.[16–18]

Some of the previous peroxyacids are commercially available and synthesized by reaction of the parent acid with hydrogen peroxide. The process can be performed on a laboratory scale, but would be subjected to severe constraints on an industrial scale. One alternative to these peroxyacids is the direct use of hydrogen peroxide as the oxidant, which provides several advantages, namely:

(a) it simplifies the process by suppressing the need to separate the carboxylic acid formed as a by-product;
(b) the high relative content in active oxygen of hydrogen peroxide makes it especially inexpensive—reagents are purchased by weight. Thus, H_2O_2 contains 45% w/w active oxygen, peracetic acid 21% and trifluoroacetic acid only 9.2%; and
(c) it produces substantially reduced amounts of by-products (water), which, in addition, are much less environmentally harmful than those derived from other peroxides.

The previous considerations have important economic implications that make hydrogen peroxide a highly attractive reagent for industrial use. In fact, chemical industries are steadily increasing their waste detoxification budgets and some production lines are bound to be thoroughly redesigned in order to comply with increasingly stringent environmental regulations.

However, hydrogen peroxide also has some disadvantages with respect to organic peroxides, namely:

(a) water is always present in the medium, both as a cosolvent and as a reaction product, and this can cause hydrolysis of the resulting esters and hinders substrate/oxidant interaction by interfering with the solvent/substrate system;
(b) hydrogen peroxide tends to easily decompose into radical species; and
(c) the reagent is kinetically inert and requires the presence of an effective catalyst to act as expected.

4. Heterogeneous catalysis in the Baeyer–Villiger reaction

4.1. Introduction

Catalysts of the homogeneous, heterogeneous and enzymatic type have been used in the Baeyer–Villiger reaction for a long time. This review focusses on heterogeneous catalysts, which provide a number of advantages over homogeneous catalysts in this context. Thus, these catalysts can modify the three-dimensionality of the ‘reaction space’ (fractal dimension), withstand high temperatures, be prepared with the desired texture and easily removed from the reaction mixture, act as inhibitors and catalyst boosters and be easily recycled and facilitate monitoring of the process.

Obviously, heterogeneous catalysts are usually less selective than homogeneous catalysts. However, the greatest weakness of heterogeneous catalysts is their low enantioselectivity, which is being improved in great strides in relation to hydrogenation reactions[19–21] and, more gradually, in other processes.[22] Catalyzed processes usually have some advantages over stoichiometric organic syntheses including shorter reaction times, higher selectivity, reduced formation of salts, milder reaction conditions and minimal use of hazardous solvents and reagents liable to poison the catalyst.

In addition, increasingly stringent environmental regulations have compelled the modification of a number of oxidation processes including the Baeyer–Villiger reaction. Traditional oxidation methods use vast amounts of highly toxic inorganic compounds such as potassium permanganate and dichromate. According to Hill,[23] the ideal ‘green’ oxidants are molecular oxygen and hydrogen peroxide in combination with recyclable catalysts in non-toxic solvents. As summarized in Figure 2, such catalysts should be highly selective and stable, and also environmentally benign.

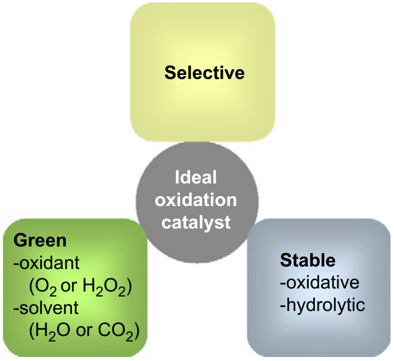


Figure 2. Ideal oxidation catalyst.[23]

As noted earlier, the catalysts for the Baeyer–Villiger reaction vary widely in nature and include acids, bases, metal complexes and enzymes. Below are discussed the most salient advances achieved with these types of heterogeneous catalysts.

4.2. Zeolite-based catalysts

4.2.1. Introduction

Zeolites are crystalline aluminosilicates consisting of a three-dimensional network of general formula $xM_{2/n}O\cdot xAl_2O_3\cdot ySiO_2\cdot zH_2O$, where M is an alkali or alkaline-earth metal and z denotes the amount of water held in the voids. A number of zeolitic compounds known as ‘zeotypes’ or ‘molecular sieves’ have been prepared containing tetrahedral Si, Al and P atoms in addition to various transition metals and elements from other columns in the periodic table such as B, Ga, Fe, Cr, Ti, Sn, V, Mn, Co, Zn and Cu spanning valencies from +1 to +5. Depending on their particular composition, these compounds are designated as $AlPO_4$s (aluminium phosphates), SAPOs (silico-alumino phosphates), MeAlPOs (metal-containing aluminium phosphates), or MeSAPOs (metal-containing silico-alumino phosphates).[24,25] The most salient structural feature of these compounds is that their tetrahedral cluster successively forms three-dimensional crystal networks containing channels and cavities of molecular dimensions (Fig. 3).

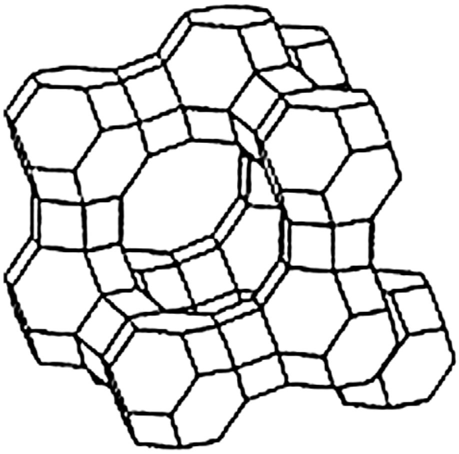


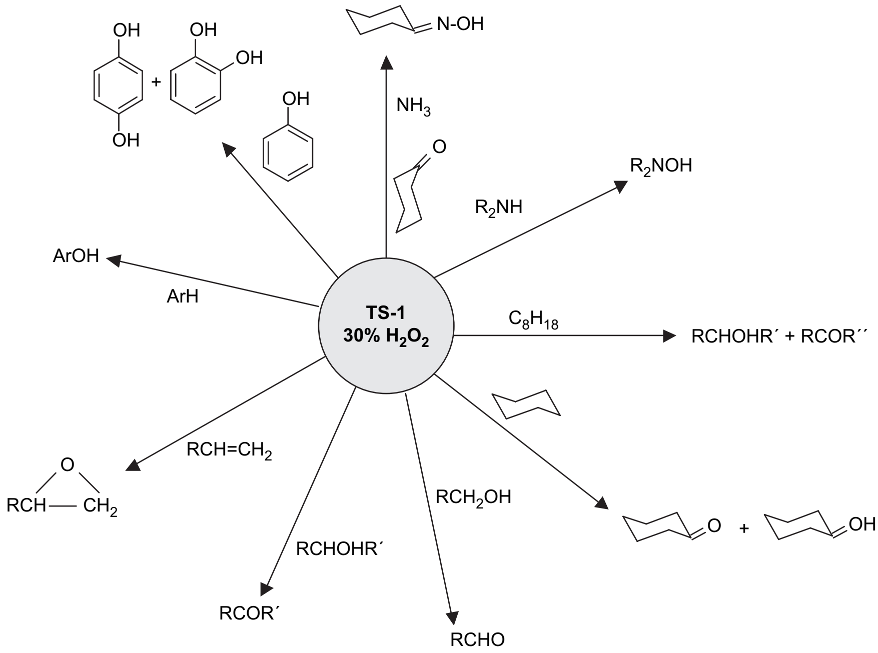
Figure 3. Three-dimensional structure of zeolite, faujasite.

A zeolite-catalyzed reaction typically involves the following steps: (1) diffusion of reactant molecules to active sites in the zeolite through its micropores; (2) adsorption at active sites; (3) chemical reaction to give the product; and (4) diffusion of the adsorbed product through channels in the zeolite.

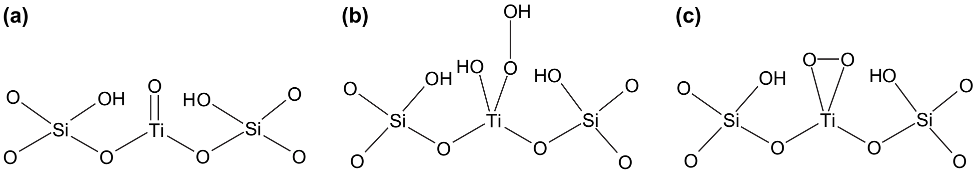
Zeolites have found a large number of uses in a variety of catalyzed processes[26,27] including oxidations and, specifically, the Baeyer–Villiger reaction. Below are discussed the most salient results obtained in this respect, depending on the nature of the zeolites used as catalysts.

4.2.2. Titanium-containing zeolites

Ever since they were discovered by Taramasso et al.,[28] titanium silicalite-based zeolites (molecular sieves) have dramatically expanded the scope of liquid-phase oxidations involving hydrogen peroxide as the oxidant. The high oxidizing power of H_2O_2 in combination with titanium zeolites is a result of the ability of titanium metal sites to form peroxo-Ti species that can activate the peroxide in various types of oxidation reactions including the epoxidation of double bonds, amonoxidations and oxidation of CH bonds.[29–31] Scheme 4 summarizes these processes.



Scheme 4. Oxidation reactions involving H_2O_2 as oxidant and TS-1 as catalyst.[31]

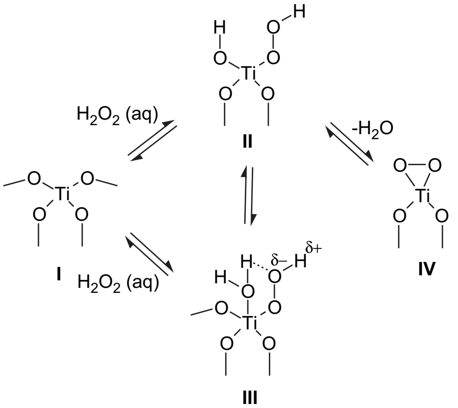


Scheme 5. Active sites in TS-1.[31]

TS-1 zeolite is Si rich and possesses a ZSM-5 structure where a small number of Ti^{IV} atoms (0.1–2.5%) have been incorporated into the three-dimensional tetrahedral network by isomorphic substitution. The Si/Al ratio is so high that the solid contains a negligible number of strong acidic sites. In accordance with Notari,[32] the active sites in this zeolite can be depicted as shown in Scheme 5a and, in fact, there is evidence suggesting that TS-1 contains an appreciable number of titanyl sites in each crystal. Each Ti^{IV} site is surrounded by four Si^{IV} atoms and isolated from other titanyl sites by Si–O–Si–O chains. According to this author, the addition of H_2O_2 to the titanium metal sites produces peroxide species in hydrated (Scheme 5b) or dehydrated form (Scheme 5c). The mechanism of this oxidation process seemingly involves the transfer of a peroxide oxygen to the substrate to be oxidized—at least in amonoxidation reactions.[33]

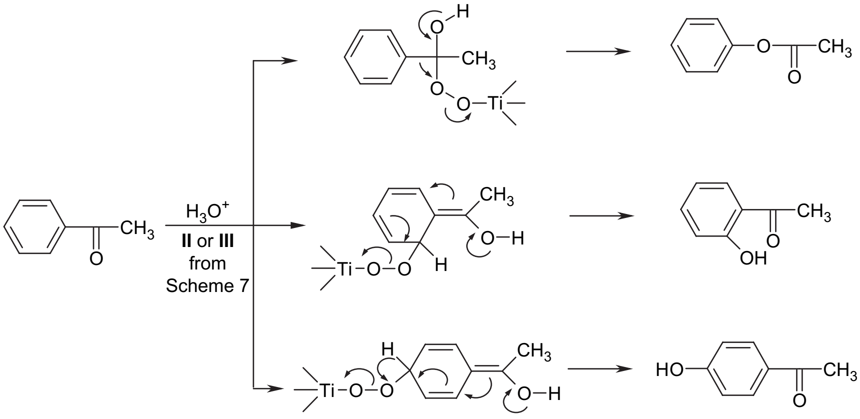
Bhaumik et al.[34] studied the Baeyer–Villiger oxidation of cyclohexanone and acetophenone with TS-1 as catalyst, using a three-phase system (ketone+H_2O_2/H_2O+catalyst) in the presence and absence of acetonitrile as solvent. The three-phase system was found to provide improved results that were even better if a small amount of sulfuric acid was added to the reaction medium. In any case, the reactions also produced variable amounts of hydroxyketones, the formation of which was favoured by the Brönsted acid character of TS-1 in the presence of H_2O; under these conditions, the solid can form ≡Ti–O–O–H peroxide species that are stabilized by a protic solvent such as water (see Scheme 6).

Scheme 7 shows a plausible mechanism for the oxidation of acetophenone and formation of the hydroxyketones in Scheme 6. Based on this mechanism, species II can act as a nucleophile (especially in the presence of water) and attack the positive carbon atom resulting from the initial protonation step, yielding benzyl acetate via the intermediate shown in Scheme 6. Similarly, species II can attack the electron-deficient carbon atoms at the *ortho* and *para* positions of the aromatic ring to give the corresponding *o*- and *p*-hydroxyacetophenones. The mechanism was subsequently confirmed by the same authors using acetophenones bearing deactivating substituents.[35]



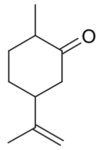
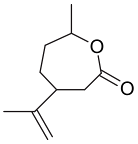
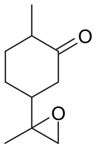
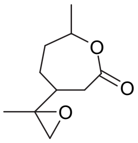
Scheme 7. Potential species formed by Ti on interaction with H_2O_2.[33]

For the previous reasons, and also because of their poor selectivity, TS-1 catalysts provide low conversions in the Baeyer–Villiger reaction, regardless of the working conditions. In fact, titanium is a poor catalyst not only in heterogeneous, but also in homogeneous media, as shown by Watanabe et al.[36] for a titanium–salen complex. This is an excellent



Scheme 6. Mechanism for Baeyer–Villiger oxidation of acetophenone with TS-1 as catalyst and formation of the corresponding hydroxyacetophenones.[34]

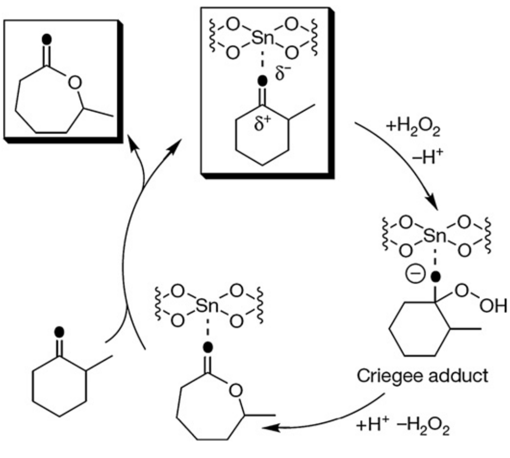
Table 1
Baeyer–Villiger oxidation of dihydrocarvone with various oxidants[37]

Oxidant	Reactant conversion (%)	Selectivity (%)		
				
Sn–beta zeolite /H_2O_2	68	100	0	0
*m*CPBA	85	11	71	18
Ti–beta zeolite/H_2O_2	48	0	79	0

catalyst in sulfoxidation reactions, but exhibits a low selectivity in the oxidation of 3-phenylcyclobutanone with hydrogen peroxide.

4.2.3. Tin-containing zeolites

Tin-containing beta zeolite has become one of the most effective catalysts for the Baeyer–Villiger reaction. This zeolite has been used for this purpose by Corma et al.,[37] early this decade, when they found it to catalyze the oxidation of adamantanone and cyclohexanone to their corresponding lactones with 35% aqueous H_2O_2 in the liquid phase at 56 and 90 °C, respectively. The selectivity towards the lactones was excellent and, additionally, the catalyst was amenable to re-use with a virtually constant activity in up to four catalytic cycles. The catalyst was also proved to be highly chemoselective in the Baeyer–Villiger oxidation of unsaturated ketones. Table 1 compares the results for dihydrocarvone as obtained with beta Sn–zeolite and beta Ti–zeolite. As can be seen, the former catalyst exhibited 100% selectivity towards the lactone and the latter towards the epoxidation of the double bond. With *m*-chloroperbenzoic acid (*m*CPBA) as oxidant, however, the selectivity towards the lactone was very low and the major product was, again, epoxide. In order to explain these results, Corma et al. used IR spectroscopic measurements of ^{18}O-labelled 2-methylcyclohexanone to develop the mechanism of Scheme 8: activation of the carbonyl group on the Sn atoms in beta zeolite, which are Lewis acids, followed by a nucleophilic attack of H_2O_2 on the carbonyl carbon to give an intermediate similar to the Criegee adduct; this rearranges to the end product, which is desorbed from the zeolite by a fresh ketone molecule.



Scheme 8. Catalytic cycle of Baeyer–Villiger oxidation of ketones with H_2O_2 in the presence of beta Sn–zeolite as catalyst.[37]

Shortly afterwards, these authors expanded their initial study in order to confirm their mechanism. To this end, they used in situ IR spectroscopic measurements, isotopic labelling[38] and theoretical methods,[39,40] and found aromatic aldehydes to be oxidized to their corresponding formates under identical reaction conditions to those for the previously studied ketones.[38,41] Based on ^{119}Sn MAS NMR measurements, they found Sn to be tetrahedrally coordinated.[38] They used these results to develop a kinetic model, which they checked against the experimental results for the structures in Scheme 9 in order to confirm the mechanism.

Finally, these authors expanded the scope of the reaction as a synthetic method for some organic compounds of interest to the aroma industry[42] and conducted an in-depth study of the catalyst surface using X-ray measurements.[43]

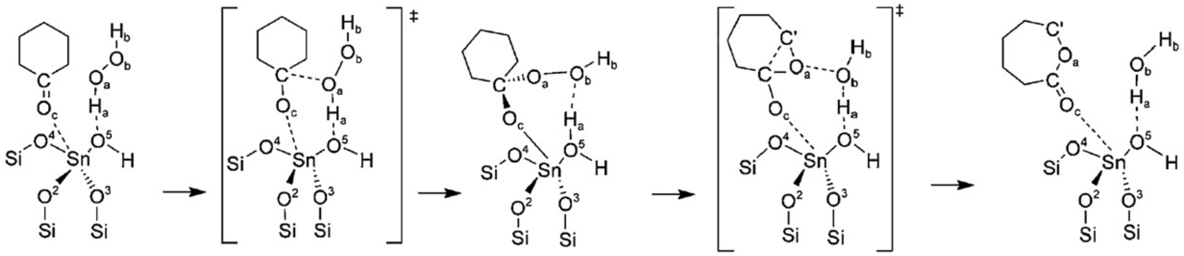
4.2.4. MeAlPOs

These microporous zeolites have been successfully used in the Baeyer–Villiger reaction by Thomas et al.,[44–48] the main difference from the previous work being the nature of the oxidant. Thus, these authors used a mixture of molecular oxygen and aldehyde for the in situ generation of a peracid in order to facilitate oxygen transfer, and inserted oxidizing metals (Mn^{III} or Co^{III}) into the MeAlPO structure (Me=Mn or Co).

By using these two metals and air or molecular oxygen in addition to an aldehyde they obtained a peracid, which they used as an environmentally benign oxygen donor to convert a cyclic ketone into the corresponding lactone. Figure 4 depicts the process for benzaldehyde. As can be seen, the aldehyde molecule can easily penetrate into the channels in MeAlPO-36 (Me=Co or Mn) and autoxidize to $PhCO^{\bullet}$ radicals, such radicals give $PhCOOO^{\bullet}$ species that undergo a series of well-established transformations leading to the formation of a perbenzoic acid, which ultimately attacks the ketone as a nucleophile and oxidizes it to its lactone.

4.2.5. Other zeolites

Acid zeolites containing no oxidizing metals (e.g., HZSM-5) have been used as catalysts in the Baeyer–Villiger reaction of cyclopentanone with hydrogen peroxide.[49] Zeolites



Scheme 9. Structures involved in Baeyer–Villiger reactions on beta Sn–zeolite.[40]

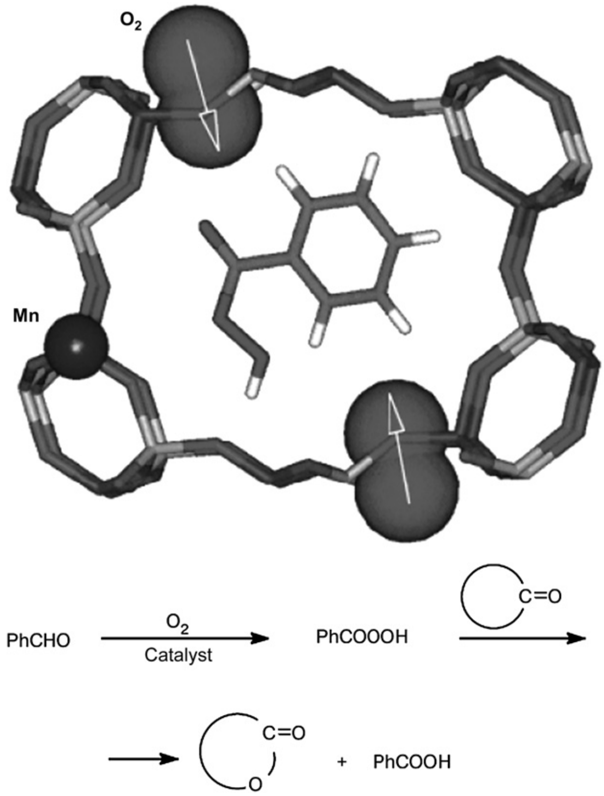
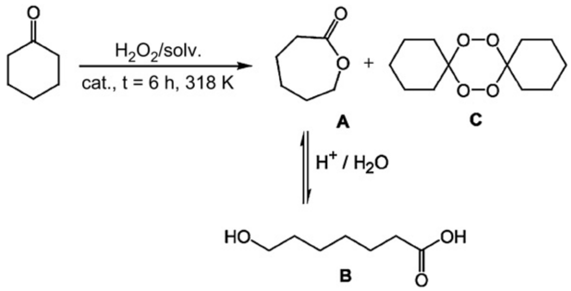


Figure 4. Graphical depiction of in situ formation of perbenzoic acid from benzaldehyde and molecular oxygen within micropores of MnAlPO-36.[47]

containing a high proportion of silicon were found to efficiently catalyze the reaction. In addition, the hydrophobicity was found to play a prominent role in the process as this occurred largely on Brönsted acid sites in the zeolite pores. A comparison of the acid zeolite with TS-1 revealed the latter to provide lower conversions of cyclopentanone into δ-valerolactone than did the former. This suggests that HZSM-5 is a better catalyst than TS-1 for the Baeyer–Villiger reaction in aqueous media. In any case, the results provided by the acid zeolite were only fairly good.

A de-aluminated beta zeolite (H-BEA) was also used as catalyst in the Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone with hydrogen peroxide.[50] The calcination temperature of the zeolite was found to have a little influence on the outcome, as the conversion was virtually identical with solids calcined at temperatures over the range 500–750 °C. Although the conversion was not too good, the selectivity for ε-caprolactone was very poor but increased with increasing calcination temperature. The low selectivity of the zeolite was ascribed to its acid sites catalyzing the production of dicyclohexylidene peroxide (product C in Scheme 10) and favouring opening of the lactone ring, which led to the formation of hydroxyacid B in Scheme 10.



Scheme 10. Baeyer–Villiger oxidation on an H-BEA catalyst.[50]

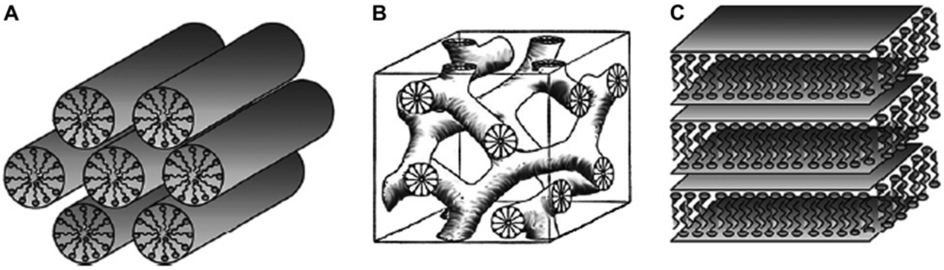
4.3. Mesoporous ordered catalysts

4.3.1. Introduction

In 1990, researchers at Mobil reported three different structures with pore sizes in the mesopore range, which they designated as MCM-M41S.[51,52] Solids MCM-41, MCM-48 and MCM-50 are the most widely used catalysts in this family. Structurally, MCM-41 consists of a block of one-way hexagonal channels resembling a honeycomb, MCM-48 of a cubic mesophase of cross-linked three-dimensional channels and MCM-50 of a layered mesophase (see Scheme 11).[25]

4.3.2. MCM-41 and MCM-48 based catalysts

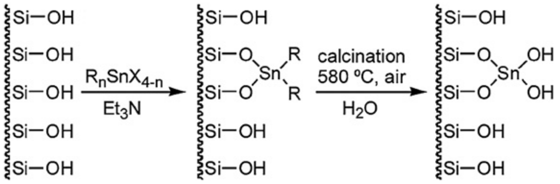
As stated in the previous section, titanium-containing zeolites are effective catalysts for oxidation reactions. Tin-containing zeolites, however, provide better results. Leaching of the metal is a common problem in reactions in the liquid phase (particularly in those involving oxidation with a peroxide by an effect of the chelating and solvolytic properties of the oxidant and products).[53] Although no evidence of metal leaching during the Baeyer–Villiger reaction appears to exist, mesoporous catalysts containing titanium have been found to release some metal during the oxidation of alcohols with hydrogen peroxide;[53] with *tert*-butyl hydroperoxide as oxidant, however, the amount of titanium leached was minimal. While titanium-based catalysts on mesoporous supports such as MCM-41 or



Scheme 11. Schematic depiction of the three mesoporous structures: (A) MCM-41; (B) MCM-48; (C) MCM-50.

MCM-48 have scarcely been used in the Baeyer–Villiger reaction, the equivalent tin-based catalysts such as Sn–MCM-41 and Sn–MCM-48 have been widely employed for this purpose.[54–58]

The use of mesoporous catalysts was chiefly intended to overcome the limited diffusion of the reactants resulting from the low microporosity of Sn–zeolite. In the new materials, Sn bonds to the solid surface via silicon sites, this allows a variety of catalysts to be prepared by changing the Sn precursor and Si/Sn ratio. Scheme 12 summarizes the bonding process of Sn from organo tin chlorides.

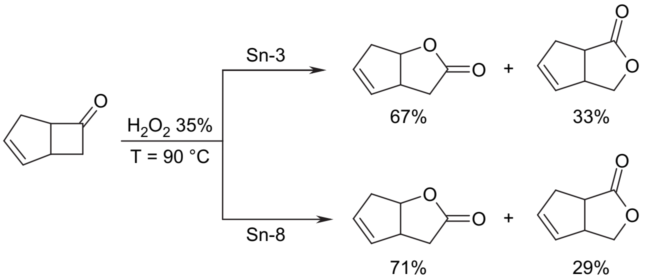


Scheme 12. Anchoring of R_nSnCl_{4-n} precursor onto MCM-41 silica, followed by oxidative elimination of organic substituent and hydrolysis.[54]

Table 2 shows the results provided by selected catalysts of this type in the Baeyer–Villiger oxidation of adamantanone. As can be seen, the conversion, turnover number (TON) and selectivity were excellent in many cases. In addition, there was a high chemoselectivity to the unsaturated lactone when the reactant was an unsaturated ketone such as bicyclo[3.2.0]hept-3-en-1-one (see Scheme 13). Other oxidizing metals such as Fe(III) have also been incorporated into mesoporous solids such as MCM-41 for use as catalysts in the Baeyer–Villiger oxidation of ketones with a mixture of oxygen and benzaldehyde as the oxidant.[59] The results were very good, but still not better than those provided by Sn–MCM-41. The mechanism for the process is similar to that proposed by Corma et al.[37] for beta Sn–zeolite catalysts.

Table 2
Preparation conditions for various Sn–MCM-41 catalysts and activity in Baeyer–Villiger oxidation of adamantanone after 7 h[49]

Catalyst	Grafting agent	SnO_2 (wt %)	Turnover number	Conversion	Selectivity
Sn-1	${}^{n}Bu_3SnCl$	1.41	163	76	>99
Sn-2	${}^{n}Bu_2SnCl_2$	1.54	173	89	>99
Sn-3	${}^{n}BuSnCl_3$	2.91	103	96	>99
Sn-4	Me_2SnCl_2	1.84	153	93	>99
Sn-5	Me_2SnCl_2	2.16	131	94	>99
Sn-6	$Sn(O^tBu)_4$	2.41	36	36	>99
Sn-7	Synthesis	1.30	219	95	>99
Sn-8	Synthesis	2.89	104	>99	>99



Scheme 13. Baeyer–Villiger reaction of bicyclo[3.2.0]hept-3-en-1-one on catalysts Sn-3 and Sn-8 (see Table 2).

4.4. Clay-based catalysts

4.4.1. Introduction

A number of layered materials with potential uses as catalysts are currently known. Such materials include cationic clays (and related silicates) and anionic clays, both of which have aroused much interest at the laboratory and industrial levels. This topic has been the subject of several excellent reviews.[60–63]

Some of the clays are natural minerals including smectite-like layered silicates (montmorillonite, beidellite, hectorite, saponite) and layered double hydroxides (hydrotalcite, pyroaurite, takovite, meixnerite) and Table 3 shows their composition. In any case, their use as catalysts has been fostered by the ability to synthesize them in the laboratory, in order to adapt their properties to specific requirements.

Table 3
Structural formulae of various clays

Clay	Formula
Montmorillonite	$Na_x(Al_{2-x}Mg_x)(Si_4O_{10})(OH)_2\cdot zH_2O$
Beidellite	$M_x(Al_2)(Al_xSi_{4-x}O_{10})(OH)_2\cdot zH_2O$
Hectorite	$(Na_2Ca)_{x/2}(Li_xMg_{3-x})(Si_4O_{10})(OH)_2\cdot zH_2O$
Saponite	$Ca_{x/2}Mg_3(Al_xSi_{4-x}O_{10})\cdot zH_2O$
Hydrotalcite	$Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$
Pyroaurite	$Mg_6Fe_2(OH)_{16}CO_3\cdot 4H_2O$
Takovite	$Ni_6Al_2(OH)_{16}CO_3\cdot 4H_2O$
Meixnerite	$Mg_6Al_2(OH)_{16}(OH)_2\cdot 4H_2O$

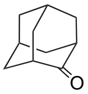
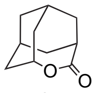
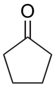
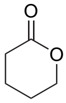
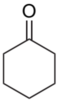
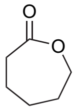
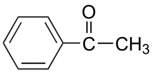
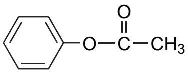
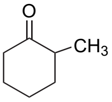
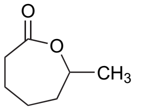
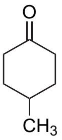
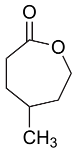
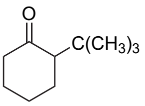
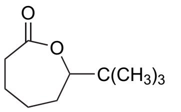
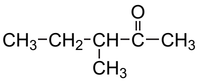
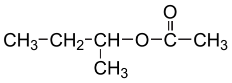
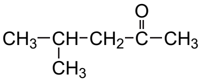
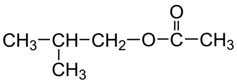
4.4.2. Cationic clays

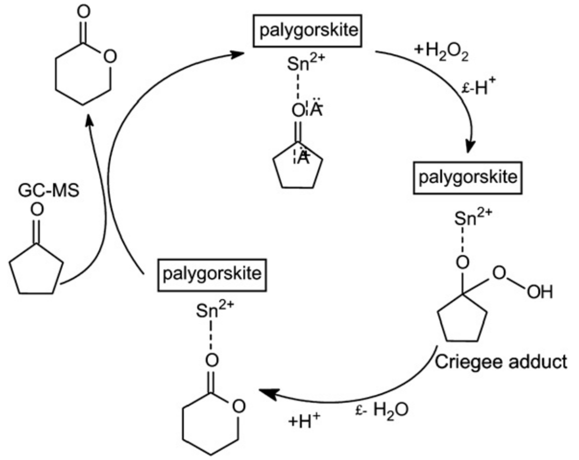
The catalytic uses of cationic clays, which date back to 1915, are very important. Thus, smectites have been used as cracking catalysts in the Houdry process for more than 50 years, but they are being increasingly replaced with zeolites, which provide better activity and selectivity. In any case, cationic clays continue to be widely used in a variety of chemical processes including dehydrations,[64,65] isomerizations,[66,67] rearrangements,[68,69] aromatic electrophilic substitutions,[70] Diels–Alder reactions[71,72] and carbon–carbon coupling reactions.[73–75] Oxidation reactions including Baeyer–Villiger oxidations have also benefited from the use of these catalysts, which, however, require the presence of an oxidizing cation such as tin to be effective. As an exception, Hirano et al. successfully used bentonite as a catalyst in the oxidation of substituted cyclohexanones with magnesium monoperoxyphthalate as the oxidant more than a decade ago.[76]

As noted earlier, tin-containing cationic clays have proved to be excellent catalysts for the Baeyer–Villiger oxidation of ketones. Specifically, Lei et al. have used palygorskite and montmorillonite as supports for Sn(II) complexes[77,78] and $SnCl_2$,[79] respectively. They found both systems to be excellent catalysts for Baeyer–Villiger oxidations. Thus, Sn–palygorskite exhibited a high catalytic activity in the Baeyer–Villiger oxidation of cyclic and acyclic ketones with hydrogen peroxide and, specifically, 2-adamantanone, 3-methyl-2-pentanone and 4-methyl-2-pentanone were nearly quantitatively converted into their corresponding lactones or esters. Table 4 shows the results obtained by these authors using 0.1 mmol of substrate, 3 mg of catalyst and a reaction time of 24 h.

Scheme 14 shows a plausible mechanism for the process, which resembles that of Sn–zeolites. Ketone initially bonds to an Sn Lewis acid site, which activates the carbonyl group. Then, it undergoes the nucleophilic attack of hydrogen peroxide on the carbonyl carbon and a subsequent rearrangement, after which process the lactone molecule formed is replaced with a fresh molecule of substrate.

Table 4
Baeyer–Villiger oxidation of various ketones in the presence of Sn–palygorskite as catalyst[77]

Substrate	Temp (°C)	H_2O_2 (equiv) (30%)	Solvent	Conversion (%)	Selectivity (%)	Turnover number	Product
	90	1.5	Nitrobenzene	100	100	164	
	70	1.5	1,4-Dioxane	81	100	132	
	70	1.5	1,4-Dioxane	16	90	26	
	70	1.5	1,4-Dioxane	37	100	61	
	90	1.5	1,4-Dioxane	80	100	197	
	90	1.5	1,4-Dioxane	44	100	108	
	90	1.5	1,4-Dioxane	25	100	31	
 $CH_3-CH_2-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CH_3$	90	1.5	1,4-Dioxane	100	100	123	 $CH_3-CH_2-\underset{CH_3}{CH}-O-\overset{O}{\overset{\|}{C}}-CH_3$
 $CH_3-\underset{CH_3}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	90	1.5	1,4-Dioxane	100	100	123	 $CH_3-\underset{CH_3}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$



Scheme 14. Mechanism for Baeyer–Villiger oxidation reactions in the presence of Sn–palygorskite as catalyst.[77]

4.4.3. Anionic clays

Anionic clays, also known as 'layered double hydroxides' or, simply, 'hydrotalcites', conform to the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{n/x}]^{n-}\cdot mH_2O$,[80,81] where M(II) denotes a divalent metal, and M(III) a trivalent metal, both at octahedral positions in the hydroxyl layers, A^{n-} is an interlayer anion, m the number of interlayer water molecules and x the atomic ratio M(III)/[M(II)+M(III)], which usually ranges from 0.2 [M(II)/M(III)=4] to 0.33 [M(II)/M(III)=2].

Hydrotalcites are structurally similar to brucite, $Mg(OH)_2$, and consist of positively charged layers of double hydroxides, interlayer spacings filled with anions that offset the positive charge of the layers and water molecules (see Fig. 5).

The most salient crystallochemical feature of the layers is that they contain heterovalent cations and are charge deficient as a result. In general, brucite-like layers consist of various ion pairs of the types M^{2+}/M^{3+}, M^{+}/M^{3+} and M^{2+}/M^{4+}, with $M^{+}=Li^{+}$; $M^{2+}=Mg^{2+}$, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, etc.; $M^{3+}=Al^{3+}$, Ga^{3+}, In^{3+}, Co^{3+}, Mn^{3+}, V^{3+}, etc.; and $M^{4+}=Mn^{4+}$, Ti^{4+}, Sn^{4+}, etc. The simultaneous presence of three, or even four, types of cations in variable proportions in a layer introduces further diversity in hydrotalcites.

These solids, and some of their derivatives, have been widely used in a wide range of catalytic processes[61,62] including Baeyer–Villiger oxidations. Unlike cationic clays, they allow the use of various oxidants including O_2/aldehyde mixtures, peracids and an H_2O_2/nitrile systems.

4.4.3.1. Baeyer–Villiger oxidations with hydrotalcites and peracids or O_2/aldehyde mixtures.

Kaneda et al.[82] used Mg/Al hydrotalcites in variable metal ratios in the Baeyer–Villiger oxidation of ketones with an oxygen/benzaldehyde mixture as oxidant. This mixture had previously been found to selectively epoxidize alkenes, even in the absence of a metal catalyst.[83] Using a ketone instead of an alkene led to the formation of the product of the Baeyer–Villiger oxidation reaction. This outcome had previously been identified by Bolm et al.,[84] but the reaction was substantially improved by the addition of catalytic amounts of hydrotalcite. Kaneda et al.[82] found a hydrotalcite containing intercalated carbonate ions and having an Mg/Al ratio of 5 and benzaldehyde as oxidant to be the optimum choice for the oxidation of cyclopentanone, and Table 5 shows selected results obtained by these authors with Mg/Al, Mg/Al/Fe and Mg/Al/Cu hydrotalcites. As can be seen, introducing a transition metal into the hydrotalcite structure resulted in a substantially improved conversion in most cases.[85,86] In addition, the three types of catalyst provided better results than the use of no catalytic materials.

In subsequent work, Kaneda's group used an Mg/Al hydrotalcite in variable metal ratios and containing different interlayer anions—which resulted in a different surface basicity—in order to develop a mechanism for the process.[87] They found the activity of each catalyst to be related to its basicity, the most basic hydrotalcites being the most active, which suggested that the active sites for the oxidation reaction were the basic sites of the catalyst. The mechanism is shown in Scheme 15. Initially, benzaldehyde is oxidized to perbenzoic acid by molecular oxygen. Then, the peracid reacts with an OH basic surface site to form a perbenzoate species, which attacks the carbonyl group in ketone. The metal alkoxide intermediate thus formed undergoes hydrolysis yielding the lactone simultaneously with the formation of a molecule of benzoic acid and the regeneration of the catalyst basic site involved.

More recently, Kawabata et al.[88] used the same oxidant system in the Baeyer–Villiger reaction of ketones, albeit in the presence of hydrotalcite as the support of metal Fe, Co, Ni

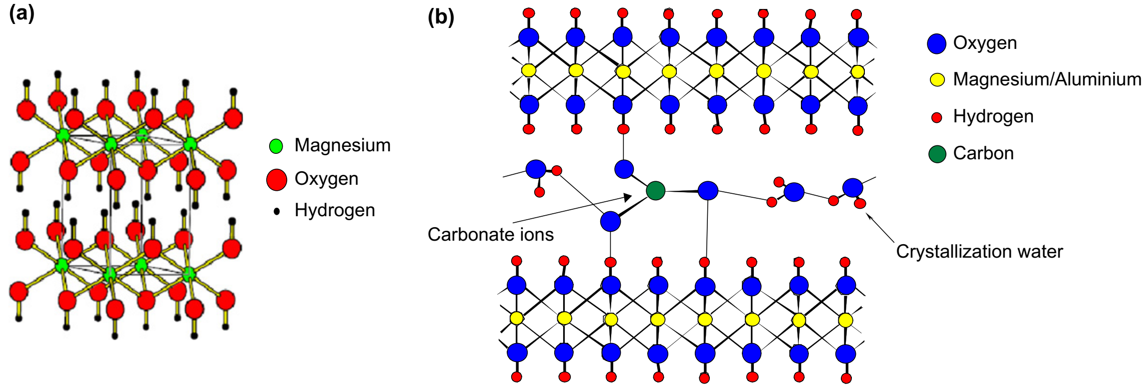
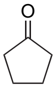
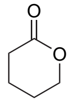
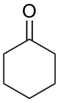
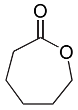
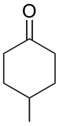
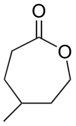
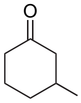
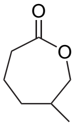
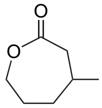
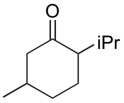
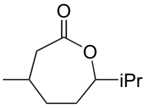
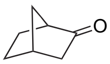
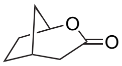
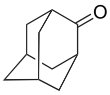
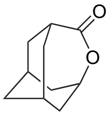
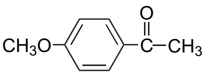
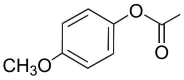
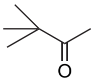
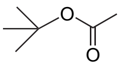


Figure 5. Structure of brucite (a) and Mg/Al hydrotalcite (b).

Table 5
Baeyer–Villiger oxidation of ketones with molecular oxygen in the presence of various hydrotalcites as catalysts

Entry	Substrate	Products	Reaction time (h)	Conv., yield (%)			
				Mg–Al–Fe–CO_3 (Mg/Al/Fe=3:1:0.3)	Mg–Al–Cu–CO_3 (Mg/Al/Cu=3:1:0.3)	Mg–Al–CO_3 (Mg/Al=3:1)	Blank (without hydrotalcite)
1			5	92, 83	60, 45	56, 46	45, 40
2			5	100, quantitative	72, 72	66, 65	83, 80
3			5	100, quantitative	73, 62	79, 79	50, 49
4		 	5	93, 93	68, 64	70, 69	57, 55
5			24	89, 89	66, 66	78, 78	32, 30
6			5	100, quantitative	100, 94	82, 70	26, 24
7			5	54, 54	100, quantitative	41, 41	43, 43
8			5	51, 51	72, 72	51, 51	
9			24	90, 88	86, 86	90, 90	16, 15
10			5	51, 45	72, 66	25, 16	
11			24	64, 57	93, 92	59, 48	43, 38

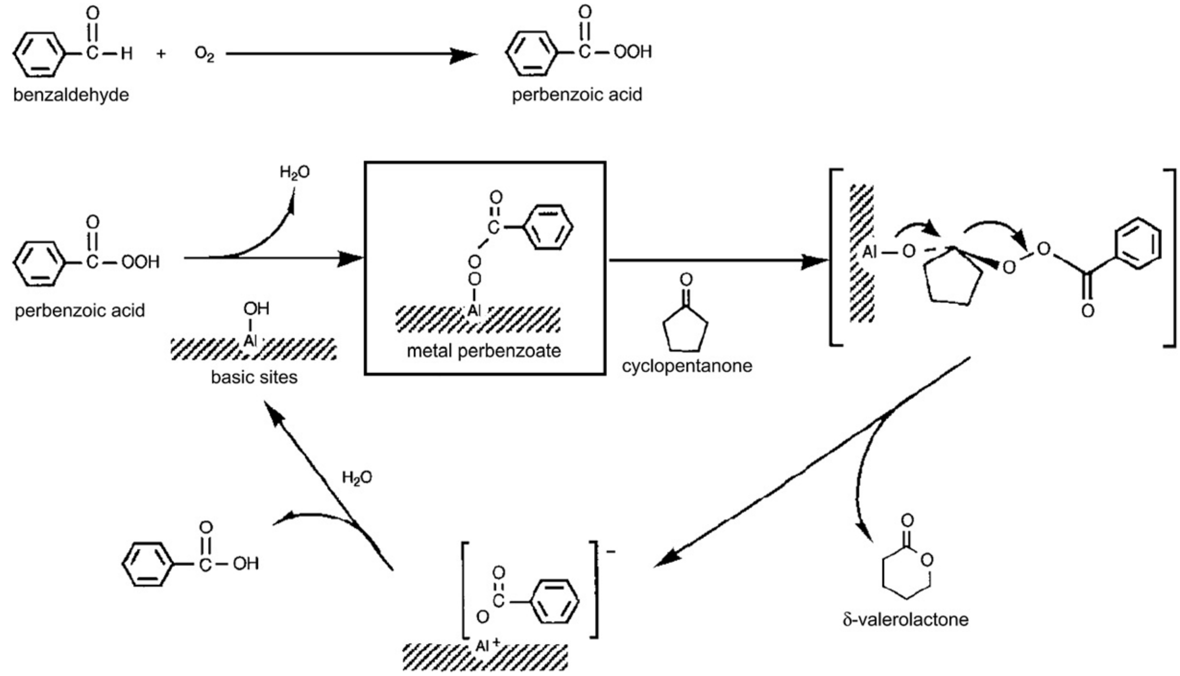
Reaction conditions: 25 mg of catalyst, 4 mmol of ketone, 12 mmol of benzaldehyde, 20 ml of 1,2-dichloroethane, T=40 °C[85]

or Cu catalysts. The results were better than those obtained with the previous catalysts, and were ascribed to the Fe^{3+}–O–Fe^{3+} clusters formed in the supported metal catalysts being more active than iron in a hydrotalcite structure.

Experiments with a peracid (e.g., *m*-chloroperbenzoic acid) and hydrotalcite-like catalysts have led to similar conclusions to those for the O_2/aldehyde system as oxidant. In fact, based on the mechanism of Scheme 15, the process is similar except for—obviously—the first step (i.e., the formation of the peracid).[87,89]

4.4.3.2. Baeyer–Villiger oxidations with hydrotalcites and nitrile/H_2O_2. The H_2O_2/peroxide system in an alkaline medium was first recognized as an oxidant for the epoxidation of alkenes more than 50 years ago.[90] More recently, Kaneda[91] and our own research group[92,93] have used mixtures of various nitriles with hydrogen peroxide in combination with hydrotalcites in the epoxidation of alkenes. With ketones as reactants, this catalyst–oxidant combination led to the Baeyer–Villiger oxidation products. Pillai[94] found a tin oxide supported on an Mg/Al hydrotalcite to catalyze the liquid-phase Baeyer–Villiger oxidation of cyclic ketones with an H_2O_2/acetonitrile system to the corresponding lactones. The specific solvent, tin content of the catalyst, reaction temperature and catalyst/substrate ratio were found to influence the final conversion of cyclohexanone into ε-caprolactone.

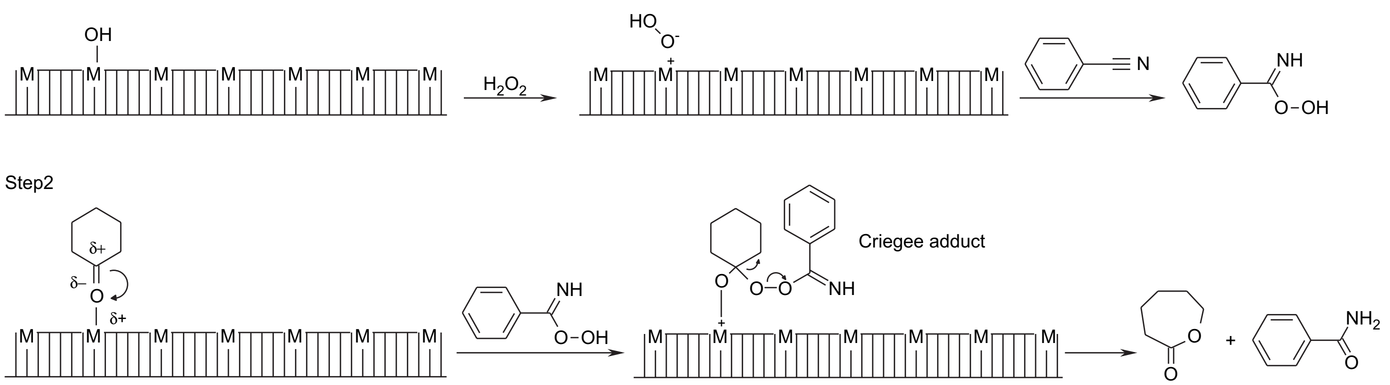
A more comprehensive study of the process involving the use of hydrotalcites was conducted by our group. Initially,



Scheme 15. Mechanism for the Baeyer–Villiger oxidation of ketones with O_2/benzaldehyde in the presence of hydrotalcites.[87]

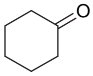
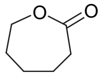
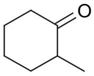
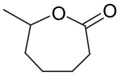
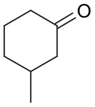
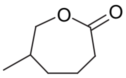
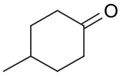
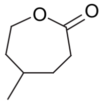
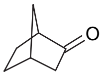
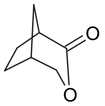
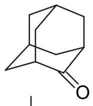
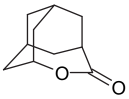
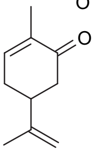
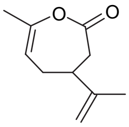
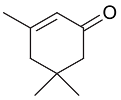
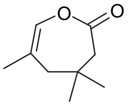
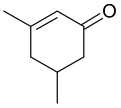
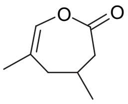
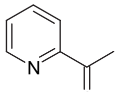
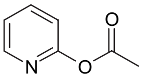
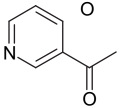
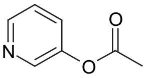
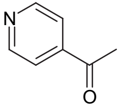
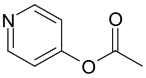
we examined the influence of the metal composition of the hydrotalcite on the Baeyer–Villiger oxidation of cyclohexanone[95] with H_2O_2/benzonitrile. Preliminary tests were performed with a large excess of nitrile and hydrogen peroxide—to ensure a zero-order kinetics in both—with a view to elucidate the role of each reactant in the process. A comparison of the results obtained with hydrotalcites of variable metal composition (viz. Mg/Al, Mg/Al/Sn and Mg/Al/Zr) revealed that those containing tin were the most active and provided better results than those obtained by using similar solids with O_2/benzaldehyde mixtures as oxidants. We proposed a two-step mechanism (Scheme 16) in which hydrogen peroxide attacks a Brönsted basic site at the catalyst surface to form a hydroperoxide species, which then attacks benzonitrile to form a peroxycarboxymidic intermediate. In the second step, the intermediate attacks a cyclohexanone molecule previously activated by adsorption at a catalyst acid site to form an intermediate resembling the Criegee adduct in homogeneous catalytic processes. Finally, the intermediate undergoes rearrangement to the corresponding lactone.

If the proposed mechanism is accepted, the Baeyer–Villiger reaction takes place at the interface between the organic and the aqueous phases in the reaction medium, with 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 favouring 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 0.6 mmol of a surfactant in the medium.[96] Both sodium dodecylsulfate (DS) and sodium dodecylbenzenesulfonate (DBS) resulted in improved



Scheme 16. Mechanism for Baeyer–Villiger oxidation reaction involving benzonitrile/H_2O_2 as oxidant and hydrotalcite as catalyst.[95]

Table 6
Conversion obtained in Baeyer–Villiger oxidation of various saturated cyclic ketones with H_2O_2 on Mg/Al hydrotalcite as catalyst[97]

Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1			100	100
2			100	90
3			100	54
4			100	100
5			100	100
6			100	100
7			64	32
8			70	26
9			71	29
10			70	100
11			96	100
12			100	100

conversion and catalytic activity, while preserving 100% selectivity.

Later, we found these catalysts to be effective with other cyclic substrates.[96,97] With 2-methylcyclohexanone (entry 2 in Table 6), they provided 89% selectivity, owing to a tertiary carbon possessing a higher migration ability than a secondary one; with 3-methylcyclohexanone (entry 3 in the table), however, the selectivity dropped to 55% as a result of the migrating ability of the two methylene groups in the α position with respect to the carbonyl carbon being similar (see Scheme 17).

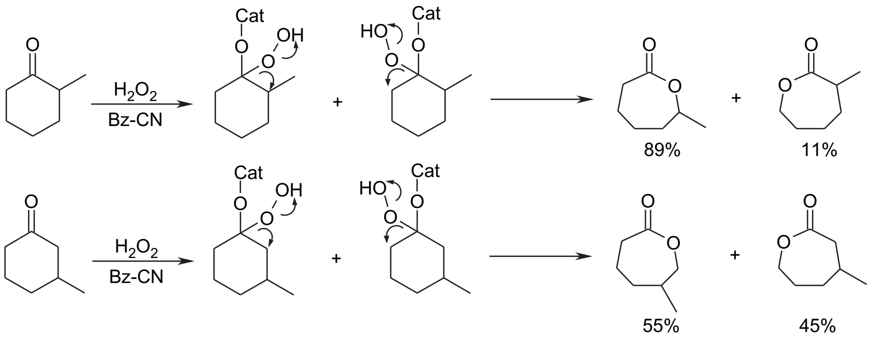
With unsaturated cyclic ketones, the oxidation system proved to be very much less selective, owing to strong competition from epoxidation of the double bonds in the substrate.

This method is, therefore, an excellent choice for conducting the Baeyer–Villiger oxidation reaction. The effects of other influential variables such as the ketone/H_2O_2/nitrile proportion, nature of the solvent and nitrile, and amount of catalyst have also been examined.[97]

4.5. Other heterogeneous catalysts

Various other types of solids have been anecdotally used as catalysts in the Baeyer–Villiger reaction. The few uses reported to date involve the following specific types:

(a) *Metal oxides*. Iron oxide[98] has been used in the oxidation of cyclic ketones with O_2/aldehyde mixtures and magnesium oxides and hydroxides prepared in different methods[99] have provided excellent conversion into ε-caprolactone in the Baeyer–Villiger oxidation of cyclohexanone with an H_2O_2/nitrile system.
(b) Resin-based acid catalysts including Nafion-H,[100,101] a perfluorinated resin and an amberlite[101] have also been successfully used in the Baeyer–Villiger reaction.
(c) *Heterogenized homogeneous catalysts*. These have opened up a booming field in catalysis, which has obviously reached the Baeyer–Villiger reaction. Thus, some catalysts bonded to or supported on solid surfaces have proved effective in this area. The catalysts include complexes of metals such as tin[102,103] or platinum[104] bonded to organic supports, and also methyltrioxorhenium supported on poly(4-vinylpyridine).[105]



Scheme 17. Criegee adducts proposed as intermediates for Baeyer–Villiger oxidation of 2- and 3-methylhexanone.

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Biographical sketch

César Jiménez-Sanchidrián was born in 1951 in Solana de Rioalmar (Spain). He studied Chemistry at the Universidad Complutense de Madrid (1967–1974), and received his Ph.D. at the Universidad Complutense de Madrid in 1977. The work was on the catalytic cracking of hydrocarbons using $AlPO_4$ as catalyst. For the last 30 years he has been working in design of catalysts and its applications at organic reactions. Actually, he is full Professor of Organic Chemistry at the Universidad de Córdoba. From 2004, he manages an investigation group working in different fields of catalysis (synthesis of nanostructured materials, plasmacatalysis, environmental catalysis, etc.). C. Jiménez-Sanchidrián has written about 180 articles on these subjects in international journals.

José Rafael Ruiz was born in Baena (Spain) in 1966 and graduated in Chemistry in 1988 and obtained his Ph.D. in 1993 from Córdoba University under the guidance of Professor C. Jiménez-Sanchidrián. He was appointed as a Professor of Organic Chemistry at the University of Córdoba in 2002. In 1993, he did a postdoctoral work with Professor F. Figueras (University of Montpellier, France) over the synthesis and application of basic catalysts in organic reactions. From 1994–1997, he worked in the Nuclear Magnetic Resonance Service of the University of Córdoba and in 1998 he returned to Organic Chemistry Department of University of Córdoba as Assistant Professor. His research interests include the development of new catalysts for organic transformations.